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# TEMPER BRITTLENESS

A Thesis
submitted for the degree of Doctor
of Philosophy in the University of
Cambridge.

by

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## Preface.

This thesis is submitted for the degree of Doctor of Philosophy in the University of Cambridge.

The research described has been carried out during the period October 1948 to October 1951, in the Department of Metallurgy, Cambridge, under the supervision of Professor G.W. Austin. My sincere thanks are due to him for his continual encouragement and many helpful suggestions.

I am also greatly indebted to Mr. G.C. Smith for many valuable discussions, and his advice on many aspects of the work.

To Dr. J. Nutting, I am indebted for all the work on the electron microscope, and his help in interpretation of the photographs.

I am very grateful to the British Iron and Steel Research Association, for a Bursary, which has enabled me to carry out the work.

I should also like to thank Mr. H. Bull of B.B. Steels Ltd., for providing the steel, on which the experiments have been performed.

The results obtained, and the theories developed are original, to the best of my knowledge, except where reference is made to other workers. No part of this thesis has been submitted for a degree at any other University.

A.R. Entwisle

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# TEMPER BRITTLENESS

## Contents.

# INTRODUCTION

The fact that phosphorus increases the brittleness of steels has been known for many years, and when the phenomenon of temper brittleness was discovered, it was soon established that the phosphorus content of a steel decidedly influenced the susceptibility to this type of brittleness. The effect of the other elements in group Vb of the periodic table, on temper brittleness has not been studied, in any detail, and it is thought that variations in the amounts of these elements (which are seldom determined) might to some extent account for unexplained variations in susceptibility, in similar steels similarly heat treated. These were often found to have different susceptibilities which could not be accounted for.

Arsenic and antimony are usually present in steels, as the results of Sullivan and Witschen[1] have shown. A summary of their analyses of twenty-one steels is given in Table I.

TABLE I

| | % Antimony | % Arsenic |
|---|---|---|
| Average of 21 steels | 0.010 | 0.010 |
| Maximum Value | 0.028 | 0.034 |
| Minimum Value | 0.001 | 0.002 |

These steels were made from American ores, which

are usually low in arsenic. Some Continental ores however, contain greater amounts of arsenic, and therefore, since the element all passes into the metal, the values given in the table cannot be considered representative for European practice. British ores are usually low in arsenic but values as high as 0.2% have been recorded.(26)

The initial aim of the work described in this thesis was to determine the effect of the group Vb elements on the temper brittleness of alloy steels. From this is developed a more general consideration of temper brittleness and the cold brittleness of steels. The study of the fractures of the steels under various conditions also proved fruitful.

# CHAPTER I

## PREVIOUS WORK.



### Temper Brittleness.

Since the beginning of this century, it has been known that some alloy steels when slowly cooled after tempering, develop poor impact properties, and that by quenching after tempering this type of brittleness could be prevented. The first comprehensive account of the phenomenon was published by Greaves in 1919(2), and this was followed by several others in collaboration with his associates at Woolwich Arsenal.(3)(4)(41) The results reported in these papers form the basis of our knowledge of the phenomenon.

The susceptibility to temper brittleness was measured in the following way:-

"Two similar samples of the steel to be examined were taken, oil hardened from 900°C and tempered for two hours at 650°C. One sample was cooled in water, and the other cooled slowly, the rate of cooling between 600°C and 400°C being uniform and 0.3°C per minute. The ratio of the impact figures of the samples was taken as expressing susceptibility under standard conditions." This method of expressing susceptibility has been used (with slight modification) by all the

early workers on the subject.

The general conclusions to be drawn from the work of Greaves are as follows:-

temper brittleness is a reversible phenomenon developed by slow cooling through the range 600°C to 400°C, or by isothermal treatment in that range, which results in low impact figures in a notched bar test. No changes in the microstructure or in the mechanical or physical properties were found to be associated with the notched bar brittleness. Increasing the chromium, manganese or phosphorus content of a given steel was found to increase the susceptibility, whilst molybdenum was found markedly to reduce the effect. Nickel was found to be deleterious when added to steels containing chromium, but without effect on plain nickel steels. Plain carbon steels (with low manganese) were found to be non-susceptible. The austenising temperature, and the subsequent rate of cooling from it were found to influence the susceptibility.

Andrew and Dickie[5] made a detailed investigation into the physical properties of tough and embrittled steels, but failed to find any marked difference, although they claimed to have detected slight differences in the microstructures. Magnetic measurements, which are very important when considering the mechanism

of embrittlement, were made by Maurer[6] without successful discrimination.

Houdremont and Schrader[7] and Bischof[8] showed that suceptibility ratio was reduced by repeated tempering above 600°C, and this was confirmed by Jones.[9] Much later, Jolivet and Chouteau[10] and Michailow-Michejew[11] showed that by increasing the tempering temperature, (above 600°C), or by increasing the tempering time, the susceptibility ratio could be substantially reduced.

In the 1930's it was found by many workers that embrittlement could be developed in most low alloy steels by long time treatments at temperatures in the region of 400°C, even in steels containing molybdenum previously thought to be non-susceptible. (see for example:- Lea and Arnold[12], Wilten[13]). This was not immediately recognised as temper brittleness and was called age embrittlement or heat embrittlement, (from the German Warmerspröding). It was established that molybdenum only retarded embrittlement in many steels and did not prevent it. Maurer, Wilms and Keisler[14], investigated the temper brittleness and heat embrittlement of a large number of experimental casts of a wide range of steels which clearly showed that the two phenomena were interrelated. They studied

the effect of molybdenum and phosphorus in some detail, but were unable to confirm the earlier hypothesis of Bennek[15], who had suggested that precipitation of phosphides was the ultimate cause of the brittleness.

Although it was realised that the testing temperature had a profound influence on the energy absorbed in the impact test (see Moneypenny[16], Bennek[15] and Wilten[13]), it was not until 1944 that it was understood that this was the crucial factor governing the measurement of the susceptibility to temper brittleness. Michailew-Michejew[11], who was the first to realise the connection with the more general phenomenon of cold brittleness, stated that:- "Temper brittleness and heat embrittlement are related, and represent a variety of the cold shortness of steels common at low temperatures." Jolivet and Vidal[17] proposed that susceptibility to temper brittleness be measured by the displacement of the temperature of transition from tough to brittle failure as between the 'tough' and 'brittle' condition. Their experimental work on a variety of chromium steels showed that in general, high susceptibility ratios (as defined by Greaves) were associated with large displacements, but that low susceptibility ratios (between 1.0 and 1.2) could give very little indication of the

displacement, except that it was probably not very great. On their more rational basis of measuring the amount of embrittlement, the importance of these observations is evident. Their work also drew attention to large effect of antimony on the susceptibility, as measured by either method.

In 1945, Hollomon produced a very comprehensive critical review of the previous work on temper brittleness, and revaluated most of the available data from this new viewpoint. The main theme of Hollomon's work was that a redetermination of the effects of alloying elements must be made in order to determine their precise effect. A detailed account of the mechanical aspects of the problem was given, but this was somewhat speculative.

Vidal[18] was the first to determine the kinetics of the precipitation on the new basis, and he demonstrated the remarkable similarity to the kinetics of age hardening systems. The most important fact he discovered was that at an embrittling temperature of 575°C regression or overageing occurred. The transition temperature, after an initial rise, decreased at long ageing times. (This was not however confirmed by the work of Jaffe and Buffum[19]). Vidal also showed that plain tungsten and molybdenum steels were

susceptible; in view of the high alloy content, and the low carbon content of these steels these results must be interpreted with some care.

Metallographic evidence of the embrittlement was first obtained by Cohen, Ulrich and Jacobsen[20], who showed that by using an etheral solution of picric acid (containing a surface active reagent), etching effects could be detected at the austenitic grain boundaries. These were found to be associated with the state of embrittlement of the steel. McLean and Northcot[21] propounded a new theory for the mechanism of temper brittleness based on metallographic evidence, which is the most generally accepted at the present time. These authors showed that a variety of reagents could be used for the detection of embrittlement, but were not able to detect the presence of individual precipitate particles. On this basis, together with the fact that no spherodisation of the precipitate occurred after very long embrittling times, McLean and Northcot suggested that embrittlement was due to the "equilibrium segregation" of carbon to the grain boundaries, without actual precipitation. The strained lattice, due to this concentration, was put forward as the embrittling constituent.

Pellini and Queneau[22] studied the effect of

structure on the transition temperatures of two susceptible steels, and showed that the displacement of transition temperature was less for pearlitic steels than for tempered martensitic steels. Their work also showed that embrittlement could proceed at temperatures up to 650°C, which is a most pertinent observation when considering the mechanism of embrittlement. Very recently, papers by Jaffe and Buffum[19] and Taber, Thornlin and Wallace[23] have provided a large amount of experimental data on the kinetics of isothermal embrittlement, and the influence of composition variables.

Jaffe and Buffum were unable to confirm the overaging reported by Vidal, but they demonstrated that embrittlement could take place at temperatures up to the Ac1 point. They also drew the conclusion that temper brittleness cannot be reduced by increasing the time of tempering at any temperature below Ac1, (up to 240 hours). This conclusion is rather misleading, as they did not study the effect of subsequent embrittling treatments. Their remarks with reference to embrittlement at high temperatures, are also open to doubt, since they fall into the error of attributing all adverse changes in transition temperature to temper brittleness. This may not be correct, as other processes can be visualised which could have the same

effect. (This refers only to the changes detected at the higher temperatures and longer times.) They also show that embrittlement takes place during continuous cooling from the tempering temperature to a greater extent than would be expected from the isothermal data. This possibly can be interpreted as meaning that nuclei which form at high temperatures can serve as sights for further precipitation at lower temperatures.

The work of Taber, Thornlin and Wallace[23] confirms the work obtained by earlier workers from room temperature tests. Chromium and manganese were found to be the most potent of the major alloying elements; nickel was found to exert a much milder effect, but the susceptibility of plain nickel steels was definitely established. More important from a practical point of view, was the fact that in general, molybdenum only reduced the susceptibility (thus confirming the work of Lea and Arnold[12] and Goodrich[24]). Fully tempered chromium-molybdenum steels, showed great resistance to embrittlement, and were found to be the best in this respect. Herres and Elsea[25] in a more limited series of experiments, showed that phosphorus exerted a real influence on the change in transition temperature due to slow cooling, and that if the amount

of phosphorous was reduced to 0.005%, the change in transition temperature was very much reduced.

Bayertz, Craig and Sheenan,[26][27] have conducted a most valuable series of experiments concerned with the effect of commercial ranges of phosphorus and molybdenum on the toughness of a 0.75% chromium steel, and a 1.5% manganese steel. These results again showed the great effect of small variations in phosphorus content in the range 0.02-0.04% P on the transition temperatures of steels slowly cooled after tempering. The effect of quite small amounts of molybdenum (0.1%) was shown to be very marked in countering the effect of the phosphorus. This work again confirmed the superior resistance of chrome-molybdenum steels to embrittlement.

The two most recent theories of temper brittleness are due to Jaffe[28] and Spretnak and Speiser[29]. Jaffe proposed that temper brittleness is due to "equilibrium segregation of carbide particles." The carbide is not specified but Jaffe states that it is unlikely to be cementite. It has been pointed out above, discrete precipitate particles were not observed, and consequently Jaffe's theory must be treated with some reserve.

Spretnak and Speiser assume that equilibrium segregation of carbon to the austenitic grain boundaries takes place while the steel is austenitic. This is

assumed to lead to retention of austenite at the boundaries on quenching. Tempering then leads to the breakdown of this austenite to give martensite, which is assumed to be responsible for the brittleness, and the intergranular fracture. This theory cannot be correct, since both the reversibility of the phenomenon, and the fact that plain carbon steels are not temper brittle cannot be explained. An earlier hypothesis due to Jaffe and Buffum, that plain carbon steels are in the temper brittle condition even when quenched after tempering, is not tenable, as has been shown by Entwisle and Smith[31]. Although the detailed mechanism suggested by Spretnak and Speiser is incorrect, grain boundary segregation during the austenising treatment is possibly a contributing factor to the brittleness.

Jacquet, in 1949 and 1950 published a series of papers on the microstructure of temper brittle steels,[32][33][34] and details of an X-ray study[35] and a micro-hardness analysis[36] on the same steels were given by Weil and Buckle. Jacquet showed that by using electro-polished specimens, in conjunction with normal etching reagents, better discrimination between 'tough' and 'brittle' specimens could be made than had been possible before. Based on his metallographic observations, and on the X-ray work and the micro-hardness tests of the other

workers, Jacquet proposed that temper brittleness is a phenomenon "which involves a reversible reaction between the carbides of various compositions, and the ferrite phase containing nickel and chromium; a reaction resulting in a state of constraint, and a critical dispersion of a part of the carbides (becoming invisible to the microscope) in the course of the embrittling reaction." However, their experimental results are open to other interpretations, since care was not taken to ensure that all specimens were tempered to the same hardness and different carbide distributions existed between them, irrespective of the embrittlement. The details given of their experimental method are very brief and it is not possible to assess the work more precisely.

Thus as a result of work published in the last seven years, a more extended view of the phenomenon can be taken. With regard to the influence of alloying elements, the earlier results are still valid, but it is now evident that the embrittlement is a more widespread phenomenon than was realised formerly, and involves the more general effect of cold brittleness. The precise identification of the embrittling phase has not yet been accomplished, although the nitride hypothesis due to Hollomon now seems unlikely.

The effect of Arsenic on the properties of Steels.

The effect of arsenic on the properties of steels has been studied in some detail. Most of the work has been confined to investigations concerning mild steels, although interest in high speed steels has been shown. Cameron and Waterhouse[37] from their own experimental work on three casts of 0.5% carbon steel, and from a study of the earlier work, came to the following conclusions:-
arsenic shows a tendency to increase the strength and hardness of steels, and to decrease the ductility. In normalised steels the strength is increased by about one ton per square inch for each 0.1% arsenic added, accompanied by a normal increase in hardness and a decrease in ductility. Arsenic causes an appreciable deterioration in the impact properties of normalised steels when present in amounts greater than 0.2%. These effects were greater in hardened and tempered steels. They concluded, that in general, "the effects of arsenic are in many ways similar to those of phosphorous, but that they do not make their appearance until the amount of arsenic present greatly exceeds the maximum allowable amount of phosphorous". Hagg[38] in 1929, investigated the systems phosphorus, arsenic,

antimony and bismuth with iron, and showed that up to about 5% of arsenic is soluble in iron at room temperature, but as pointed out by Cameron and Waterhouse, when carbon is present the solubility is considerably reduced. They estimated that no more than 0.2% is soluble in austenite in the presence of carbon. This means that amounts greater than this will tend to segregate to head of the original ingot, and be lost in the cropping. The amount of arsenic in wrought steels cannot therefore exceed this amount greatly. The most recent investigation of iron-arsenic alloys is that of Houdremont, Bennek and Neumeister[39] who investigated a wide range of carbon and low alloy steels, and studied the effects of heat treatment and strain ageing. Besides these laboratory melts, they also investigated segregation of the element in some basic Bessemer ingots, but found no excessive segregation. Their experiments on the impact properties of mild steels show that the transition temperature in the impact test was raised by additions of arsenic. The results are shown in Fig. I for a 0.15% carbon steel, normalised from 920°C. It is also apparent that the maximum impact value is decreased by the arsenic additions. With regard to the alloy steels investigated, Houdremont et alia came to the conclusion that the properties of high grade heat

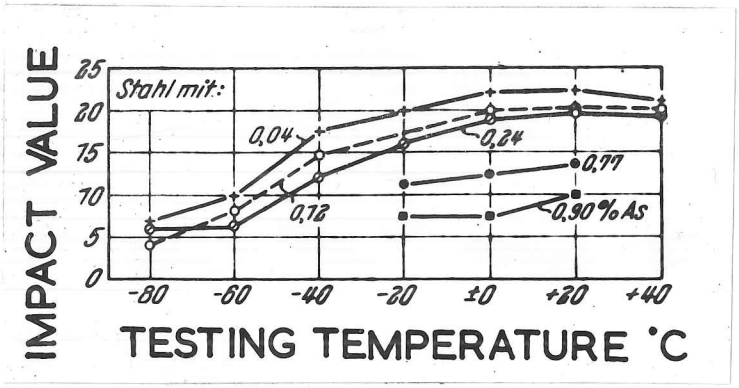


Fig. 1 (from 39)

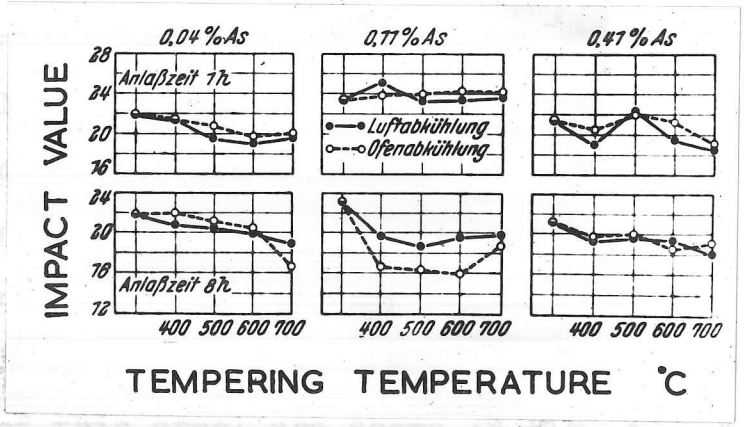


Fig. 2 (from 39)

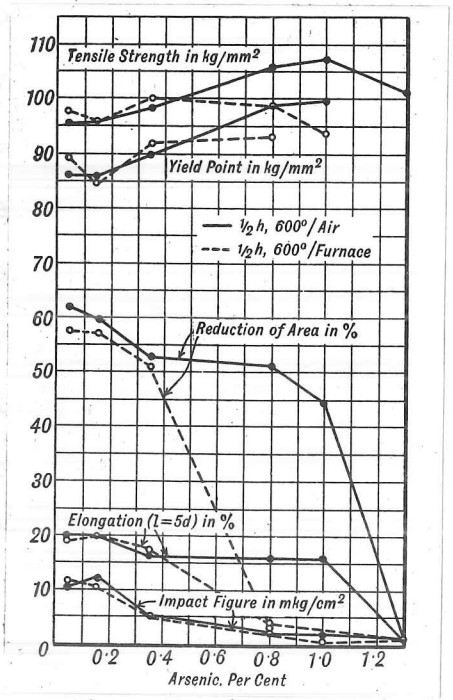


Fig. 3 (from 39)

treated alloy steels suffer greater deterioration for a given arsenic addition than do plain carbon steels. The effects were first noticeable in the reduction of area and the impact value.

A chromium-molybdenum steel (0.4% C., 0.4% Mn., 0.02% P., 0.88% Cr., 0.4% Mo.) was reported as being susceptible to temper brittleness, and the impact figures after various heat treatments are shown in Fig. 2. The initial condition of the steel was:-
normalised from 900°C, tempered 2 hrs. at 700°C. In view of the fact that a Ni-Cr steel was not reported as susceptible it must be assumed that the furnace cooling treatment (of enabkühlung) was not sufficiently discriminating. The effect of arsenic on the properties of this steel are shown in Fig. 3. These results show that for amounts of arsenic greater than 0.2%, the impact value is very low irrespective of the rate of cooling after tempering, but that the reduction of area and the elongation in the tensile test are both very much reduced by slow cooling after tempering.

It may be concluded therefore that arsenic increases the susceptibility of steels to cold brittleness, and possibly increases the susceptibility of alloy steels to temper brittleness.

The Effect of Antimony on the Properties of Steels.

Very little work has been reported on the effect of antimony on the properties of steels, although there are a few references to the properties of cast irons containing antimony. French and Digges[40] tested low tungsten, high vanadium high speed steels and concluded that antimony adversely affected the hot working properties, but had no influence on the hardness. Jones and Morgan[41] were the first to carry out a systematic investigation of the properties of mild steels containing antimony in the range 0-10% Sb. (Hagg[38] reports the solubility of Sb as 7% at ordinary temperatures) Their base material contained 0.16% C, 0.7% Mn, 0.0375% S, 0.04% P, and 0.3% Cu. Jones and Morgan's results show that like phosphorus and arsenic, antimony embrittles steel when present in sufficient quantity. The impact properties give the first indication of the presence of the element, the energy absorbed falling to a very low value when amounts greater than 0.2% are present. The strength increases only slightly up to 0.8%, and then falls more rapidly to about half the original value, at 2%. The elongation and reduction of area fall steadily with increasing antimony above 0.2%, and become zero at 1.5%. The overall effect of the antimony is similar to that of phosphorus and arsenic, but milder

in its action.

The only reference to the effect of antimony on the properties of low alloy steels is made by Jolivet and Vidal[17] who in their investigation of the temper brittleness of low chromium steels studied the effect of 0.08% Sb on the impact properties. The composition of the steel was:-

0.26% C, 0.32% Si, 0.33% Mn, 1.45% Cr, 0.012% S, 0.011% P, and 0.08% Sb. This steel was oil hardened from 875°C, and tempered 1 hr. at 650°C, and water quenched. Some of the specimens were embrittled for 24 hrs. at 525°C. The effect of the 525°C treatment on the impact properties is shown in Fig. 4. Curve 1 relates to the 'tough' steel, and curve 2 to the embrittled steel. The very large difference in the transition temperatures is unique, the material being so brittle in state 2, that even at 500°C the impact value is still very low. Jolivet and Vidal found that the most convenient method for following the embrittlement, was by tests performed at 525°C, taking the specimens straight out of the embrittling furnace and testing immediately. A similar steel, not containing antimony, was found to have a displacement of the transition temperature of only 55°C when tested after similar heat treatments. Comparison of the curves for the two steels in the un-embrittled

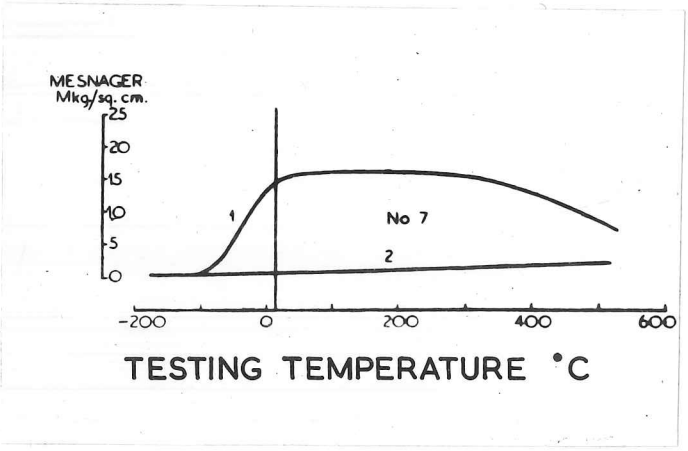
MESNAGER
Mkg/sq. cm.
25
20
15
10
5
0
1
2
No 7
-200
0
200
400
600
TESTING TEMPERATURE °C

Fig. 4 (from 17)

condition indicates that antimony raises the transition temperature by 35°C, and lowers the maximum impact value by about one third. It would therefore be expected that the effect of the antimony would be apparent in the tensile test. No other physical properties were reported by Jolivet and Vidal.

The effect of arsenic and antimony on the properties of steel it can be concluded, are similar to that of phosphorus. Antimony greatly increases the susceptibility of low alloy steels to temper brittleness, and arsenic probably has a similar, but less marked effect. The other element in Group V, Bismuth, is insoluble in steel.

# CHAPTER 2

## NOTCHED BAR TESTING AND TEMPER BRITTLENESS.

As the only mechanical test which has been used to discriminate between 'tough' and 'brittle' specimens of the same alloy steels is the notched bar test, it is necessary to consider the theory of notched bar testing, in order to appreciate the significance of the test results. The interpretation given here is based on that of Orowan[43], but the earlier work of Ludwig[44] and Kuntze[45] and a more recent theory by Holloman[46] are considered.

### Early Hypothesis.

Ludwig assumed that the mechanical behaviour of ductile metals was determined by the yield stress Y, and the strength S, and their dependence on the plastic strain e. He further assumed that the yield stress would increase with strain, more rapidly than the strength. Normally, for a ductile material, Y is less than S, and the metal yields when subjected to a uniaxial tensile stress. As plastic deformation proceeds, Y increases with respect to S, until fracture takes place when $Y_{(ef)}$ becomes equal to S at some strain $e_f$. Figure 5 presents the hypothesis in graphical form. The point F, where the S-e curve is crossed by the Y-e curve

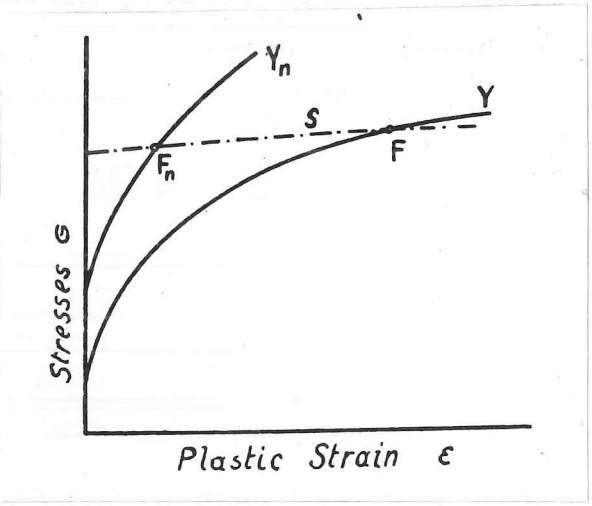
$Y_n$
Y
S
$F_n$
F
Stresses σ
Plastic Strain ε

Fig. 5

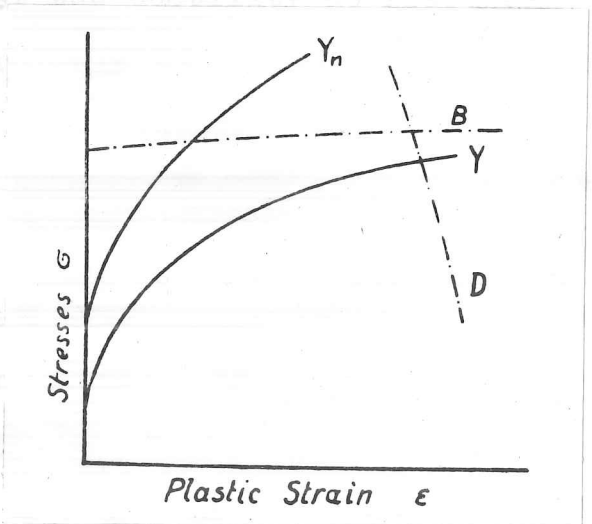
$Y_n$
B
Y
D
Stresses σ
Plastic Strain ε

Fig. 6

indicates where the metal fractures (at strain e).

Ludwig pointed out that the essential feature of notched bar tests is the triaxial state of stress at the base of the notch, (and not the high macroscopic strain rate, as had been previously inferred). This triaxial state of stress allows a high tensile stress Yn to arise towards the centre of the specimen, much greater than the yield stress Y, such that Yn = Y + R, where R is the transverse stress across the specimen. The curve Yn-e is then obtained from the Y-e curve by addition of the transverse stress R (see Fig. 5). It will be seen that the point of fracture Fn occurs at a lower value of the strain, due to the transverse stress R. The greater this stress (deeper or sharper notch) the lower the ductility at fracture. Ludwig's hypothesis therefore, accounts for the lower ductility of notched bars.

Davidenkov[47] realised that Ludwig's hypothesis did not account for the physical differences between the fractures of steels at high and low strains (due to the transverse stress). The brittle fracture obtained with deeply notched bars showed bright 'crystalline' facets, whereas the ductile fracture of smooth bars had a dull 'fibrous' appearance. Moreover, there was found to be no continuous transition between the two types, the

borderline fractures having a part fibrous and a part crystalline. He suggested that there were two strength-strain curves corresponding to the two types of fracture; one B for brittle fracture, and another D for ductile fracture. He assumed that in the absence of a notch the curve Y cuts the curve D, at a large strain and results in a ductile fracture. In the presence of a notch, the curve Yn meets the curve B at a low value of the strain, associated with the bright crystalline fracture. The modification introduced by Davidenkov is shown in Figure 6. For metals which do not exhibit brittle fracture it was assumed that the curve B occurred at much higher values of the stress, and consequently the curve D was always crossed first. Orowan has pointed out however, that fibrous fracture does not occur at definite values of the highest principal stress, and that therefore the curve D does not exist. In the absence of a sharp notch, the Yn curves end in points, the locus of which is not a curve. With a sufficiently sharp notch the Yn curve may intersect the curve B, and then brittle failure occurs.

Orowan's Theory of Notch Brittleness.

From the viewpoint outlined above, Orowan develops the criteria for the ductile or brittle behaviour of metals. The most important factor to consider is that only a few

metals are susceptible to notch brittleness (Iron, Zinc, Titanium, and their alloys). Using the Davidenkov hypothesis it is impossible to explain why, in the presence of a sufficiently sharp and deep notch it is not possible to produce brittle failure in all metals. Kuntze, who performed many experiments with notched bars with a view to determining the strength curve S, (Fig. 5) assumed that the mean constraint factor could increase to infinity if the notch was sufficiently sharp and deep. The mean constraint factor is defined as the ratio of the mean axial yield tension Yn, in the metal under the notch, to the uniaxial yield stress Y. Orowan's most important contribution to the theory of notch brittleness was to show that the maximum value of the mean constraint factor is not infinity, but is only of the order of three in a ductile material. Thus, since no crack or notch can raise the maximum tensile stress above 3Y, a material can show notch brittleness only if its brittle strength B, at a stage of plastic deformation, becomes less than about 3Y. If the brittle strength is always greater than 3Y, no brittle fracture can take place. This seems to be the case with most very ductile metals. (It is assumed in this argument that the tests relate to one temperature only.)

The ductility properties of metals can then be

said to depend on the relative magnitudes of the yield stress Y (in tension), and the brittle strength B in the following manner:-

(a) If B is less than Y, the material is brittle.

(b) If B is greater than Y, but less than 3Y, the material is ductile in uniaxial tension, but notch brittle.

(c) If B is greater than 3Y, the material is fully ductile.

Transition Temperature in Notched Bar Impact Tests.

A notched bar impact test measures the work required to fracture a standard specimen, under triaxial stresses and at a high strain rate. As has been shown above, the fracture may be brittle or ductile depending on the relative values of B and Y. For certain metals, when the work to fracture the specimen is plotted as a function of temperature, it is found that above a more or less well defined temperature, (called the transition temperature), the work required has a high value, and the fracture is fibrous; below this temperature the work required has a low value, and the fracture is brittle (crystalline). As the temperature is lowered through the transition range an increasing proportion of the surface of the fracture becomes brittle at the

expense of the fibrous part.

The reason for this sudden drop in energy absorption is explained in Figure 7, where the brittle strength B, and the yield stress Y, are plotted as functions of the testing temperature. The curve Y-T relates to a simple tension test, and the curve 3Y-T to a notched bar impact test, with a mean plastic constraint factor of 3. The brittle strength is thought to be relatively insensitive to both temperature and triaxial stresses. Above temperature $T_2$, B exceeds both Y and 3Y, and the metal behaves in a ductile manner, with high energy absorption to fracture, and with the fibrous appearance of the fractured surface. (In a tensile test this appears in the centre of the cup and cone.) At temperature $T_2$, the brittle strength becomes equal to 3Y, and brittle fracture can occur in the notched bar test, but as B still exceeds Y, the metal is still ductile in uniaxial tension. Below $T_1$, the metal is brittle in both tests. For test conditions with intermediate values of K, the transition temperature in the test will lie between $T_1$ and $T_2$. For example, in the case of a thin walled hollow cylinder subjected to internal pressure, where the surface is subjected to a balanced biaxial tension, k has the value 1.15. The metal will still be ductile in torsion, for in this case k can be

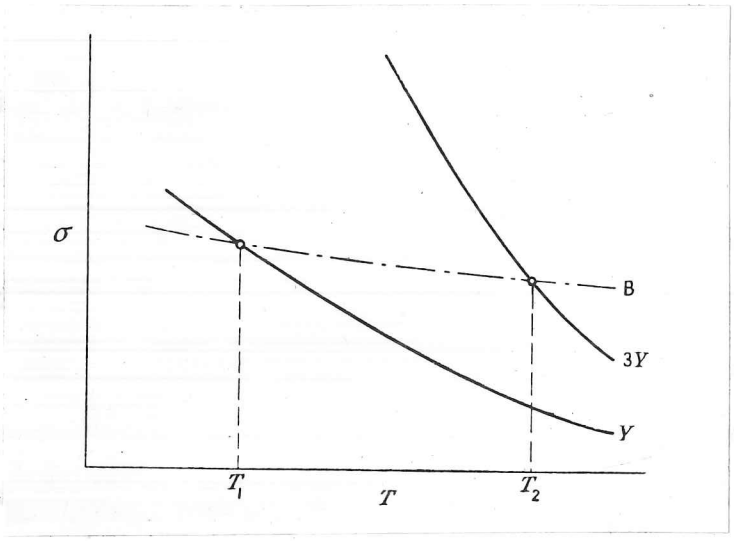
σ
B
3Y
Y
T1
T
T2

Fig. 7

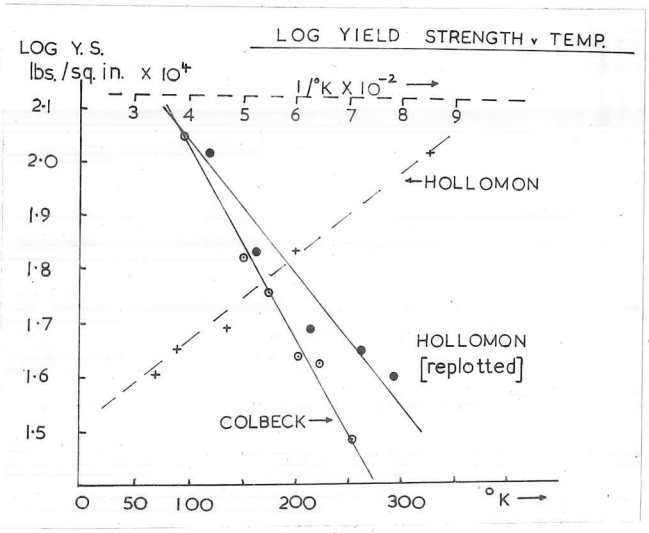
LOG YIELD STRENGTH v TEMP.
LOG Y. S.
lbs./sq. in. X 10⁴
1/°K X 10⁻²
3
4
5
6
7
8
9
2·1
2·0
1·9
1·8
1·7
1·6
1·5
HOLLOMON
HOLLOMON
[replotted]
COLBECK
0
50
100
200
300
°K

Fig. 8

considered to be 0.5, since the maximum tensile stress is half the maximum shearing stress.

In this way, Orowan's theory is able to account for the major features of the phenomenon of notch brittleness. As yet very little is known about the brittle strength of metals, and how it is influenced by mechanical and metallurgical variables. It is to be noted that at best, the theory is only an approximation, since in cases where the stresses are triaxial, it is not sufficient to describe the behaviour of the material by considering the stress and strain in the direction of one of the principal axes. As is shown later, the theory is useful in correlating test results, and useful predictions can be made, for the planning of experiments.

Hollomon's Theory

Hollomon approaches the problem from another point of view. He attributes the brittleness of notched bars to the high microscopic strain rate at the base of the notch, in combination with the stress concentration. Two assumptions which he makes in the semi-quantitative analysis given in (46) have been shown to be incorrect by Orowan. Hollomon assumes that the mean plastic constraint factor can rise to very large values with sufficiently sharp and deep notches, and also he assumes that there is only one Strength-Strain curve as

originally postulated by Ludwig. He further assumes that there is an exact equivalence between the strain rate and the testing temperature, which may not be true in all cases, although it appears that it is a reasonable approximation for steels at normal and sub-normal temperatures.

Hollomon makes no fundamental distinction between ductile fracture and brittle fracture, and his theory leads to the conclusion that both in the tension test and in the notched bar test, there is a continuous transition from one type of fracture to the other. He was not able to show that this was the case. It appears that as the ductility is reduced by altering the test conditions there is a distinct range of values of strain, between the fibrous and the crystalline fractures, in which fracture does not occur; i.e. at some value of the strain, the ductility falls precipitously.

Despite these objections, the theory does account for the phenomena associated with notched bars with some accuracy.

Conclusions.

Neither of these theories which have been described can account satisfactorily for either the size effect, which is so important when relating impact tests to the properties of engineering structures, or why the

slope of the energy absorption - temperature curve in the range in which the transition from tough to brittle failure takes place, varies with the material tested and the depth and sharpness of the notch. The greater the stress concentration, or the greater the dependence of the yield stress on the temperature, the smaller the range of temperature. For zinc and pure iron, the range is only a few degrees centigrade, but for low alloy steels, the range may be as much as forty or fifty degrees. For pearlitic steels, the temperature range increases with increasing carbon content[58] but this is probably due to the effect of the carbon on the yield stress - temperature relationships.

The results of a series of notched bar impact tests over a range of temperature are characterised by three parameters:-

(1) The Maximum Impact Value. This is the energy absorbed in fracturing (or bending) the specimen at temperature above the transition range. It can be correlated with the reduction of area in the tensile test performed at the same temperature (see for example Rinebolt and Harris[58]).

(2) The Transition Temperature. This is some measure of the temperature at which the transition from tough to brittle failure takes place. It gives an

indication of the relative values of the yield stress and the brittle strength. (This is sometimes referred to as the cohesive strength.)

(3) The Slope of the Energy Absorption-Temperature Curve in the Transition Range. For any specified test this seems to correlate with the temperature dependence of the yield stress. It may be noted here, that it is only because quenched and tempered low alloy steels have a wide transition range that the room temperature impact tests were so useful in giving a measure of the amount of embrittlement. If the transition range were sharp, (as for pure iron), room temperature impact tests would only indicate whether embrittlement had taken place, and not the extent of the reaction.

A Quantitative Interpretation of Orowan's Theory, and its Application to Temper Brittleness.

The application of Orowan's theory is much simplified if it is possible to express the yield stress and the brittle strength as definite functions of the temperature. It is then possible to obtain an expression relating the transition temperature to the brittle strength, assuming that the yield stress is known.

It is first required to obtain a suitable function

for the effect of temperature on the yield stress. Hollomon uses a relationship of the type:-

$$\text{Yield Stress} = Ae^{\left(\frac{B}{T}\right)} \qquad (1)$$

where T is the absolute temperature, R is the gas constant, and A and B are constants. He also assumes the equivalence of strain rate and temperature, and relates them through the activation energy B. McAdam[48] prefers another relationship of the type:-

$$\text{Yield Stress} = A \ln.\left(\frac{B}{T}\right) \qquad (2)$$

Both of these equations seem to be equally successful in expressing the available data for metals at temperatures below that at which recovery becomes appreciable. Hollomon's equation implies an infinite yield stress at the absolute zero, whereas McAdam's suggests a limiting value. Neither of these equations appears to have any fundamental significance, both merely being convenient methods of expressing the experimental results. It has been found possible to use another relationship for expressing the effect of temperature on the yield stress, which simplifies the subsequent analysis. This relationship is:-

$$\text{Yield Stress} = Ae^{-BT} \qquad (3)$$

where T is the absolute temperature, A and B are constants,

and e is exponential function. Fig. 8 shows three lines expressing the variation of yield stress with temperature. Hollomon's result[49] are plotted as log.yield stress-$\frac{1}{T}$, and as log.yield stress-T. Some results taken from Colbeck, McGillivray and Manning[50], for Fig. 8 Armco iron are also plotted, as log.yield stress-T. Hollomon's results refer to a low carbon steel. Together with various other data cited by Teed[51], for different carbon and low alloy steels, it can be shown that equation (3) expresses the variation of yield stress with temperature in the range of 0-300 degrees absolute with some accuracy.

The effect of temperature on the brittle strength has not been studied directly, except in a few cases. The work of De Haas and Hadfield[52] on Armco iron, and Boas and Schmid[53] on bismuth indicates that the brittle strength is relatively independent of temperature. There is other indirect evidence to support this. The brittle strength is thought to be a function of Young's modulus, the interatomic distance, and the surface energy; all these are but slightly dependent on the temperature. It is proposed to use an expression of the same type as that used for the yield stress, to express the temperature dependence of the brittle strength.

Assuming that equation (3) gives a sufficiently accurate representation, it follows that:-

$$\text{Yield Stress } (Y) = Ae^{-BT}$$

$$\text{Brittle Strength } (S) = Ce^{-DT}$$

where A, B, C and D are constants.

From Orowan's theory, the transition temperature in a notched bar test occurs when:-

$$k \times Y = B$$

where k is the mean constraint factor, and is taken to include the effect of the macroscopic strain rate. Hence:-

$$kAe^{-BT} = Ce^{-DT}$$

where in this case, T is the transition temperature.

i.e. Transition Temperature (T.T.) = $\frac{1}{D-B} \ln \left(\frac{C}{kA}\right)$

Assuming that B is very much greater than D, this reduces to

$$\text{T.T.} = \frac{1}{B} \ln \left(\frac{kA}{C}\right) \qquad (4)$$

or, the transition temperature is proportional to the log. (the brittle strength).

In this case of course, the transition temperature is taken to be the highest temperature at which complete brittle failure takes place. This definition, which is required by the assumptions made earlier is not

critical, and provided that the same definition is used throughout, for all tests, the approximations involved are not greater than the uncertainties in the other assumptions.

Equation (4) can be shown to relate tensile and notched bar tests where sufficient data are available. Thus, Petch[54] has shown that the brittle strength of ingot iron, Swedish iron and mild steel is related to the ferrite grain size by the following equation:-

$$S. = F\ell^{1/2} \quad (=c) \qquad (5)$$

where $\ell$ is the mean ferrite grain diameter in mms., and F is a constant. Substituting in equation (4).

$$T.T. = \frac{1}{B} \ln.\left(\frac{kA}{F\ell^{-1/2}}\right)$$

$$= \frac{1}{B} \ln.\left(\frac{kA}{F}\right) + \frac{1}{2B} \ln.(\ell) \qquad (6)$$

Taking the results of Petch, (for F), and those of Colbeck et alia (for A and B), and assuming that the yield stress is approximately constant with respect to the ferrite grain size provided that $\ell$ is less than 0.1 mms., (see Edwards and Pfeil[55]) the constants can be calculated, and the equation reduces to:-

$$T.T. = 288 \log_{10}\left(8.2k\right) + 144 \log_{10}(\ell) \qquad (7)$$

Hodge, Manning and Reichold(56) have determined the

effect of ferrite grain size on the transition temperature of a mild steel, and a 3% nickel steel. The results of their work for the mild steel are expressed by the equation

$$T.T. = 75-30N$$

(Charpy test, keyhole notch, T.T. in degrees F.)

where N is the A.S.T.M. grain size number. When this is converted to the units used in equation (7), it is found that

$$T.T. = 347 + 110 \log_{10}(\ell)$$

If k is taken to be equal to 2, then equation (7) reduces to

$$T.T. = 347 + 144 \log_{10}(\ell)$$

(For the keyhole notch, this value of k is probably accurate)

These results show that the calculations are sufficiently accurate to justify confidence in the initial assumptions, and in any predictions made from them. The value of k will depend on the precise test conditions, and on the two tests compared; provided that some value of this can be obtained data can be converted from one test to another.

It is interesting to note that the transition temperature of the 3% nickel steel has the same dependence

on ~~temperature~~ grain size, but at lower values of temperatures. This means that B is unaffected by the presence of the nickel, but that the relative values of A and F are changed (see equation (6)). Since nickel increases the yield stress, it must also increase the brittle strength in greater proportion; that is, A/F decreases. It is only by notched bar tests of this kind that the effect of alloying elements on the brittle strength of steels which are not brittle in tension at low temperatures, can be determined.

Considering temper brittleness, mechanically speaking the effect of the transformation is:-

(a) the transition temperature in a notched bar test is raised;

(b) the yield stress is unaltered;

(c) the dependence of the yield stress on temperature is unaltered.

(a) and (b) are well substantiated, and the results of Weister[57], who carried out low temperature tensile tests on steels which were probably temper brittle indicate that (c) is true.

Referring to equation (4)

$$T.T. = \frac{1}{B} \ln.\left(\frac{kA}{C}\right)$$

A and B are unaffected by temper brittleness, and therefore

the phenomenon is a manifestation of the lowering of the brittle strength (since the transition temperature is lowered). Separating the constants, the equation reduces to:-

$$T.T. = G - H \log.(C) \qquad (8)$$

where G and H are constants.

Also, since for a tension test

$$T.T. = \frac{1}{B} \ln.\left(\frac{A}{C}\right)$$

combining with equation (4)

$$\Delta T = \frac{1}{B} \ln.(k)$$

where $\Delta T$ is the difference in transition temperature between a notched bar test and a tension test.

As $\ln.(k)$ is approximately equal to unity for sharp notches ($\ln.(k)$ ranges from 0.9555 to 1.0986 whilst k is in the range 2.5 to 3.0), this can be further simplified:-

$$\Delta T = \frac{1}{B} \qquad (9)$$

For ferritic steels, 1/B varies between approximately 120 for pure iron and 700 for quenched and tempered highly alloyed steels. It is greater for quenched and tempered steels than for pearlitic steels, and may also depend on the amount of pearlite in the pearlitic steels.

Referring to equation (9), it is seen that for steels with the same notched bar transition temperature, (say $0^{\circ}C$), then the tensile properties at the temperature of liquid air will depend very much on the temperature dependence of the yield stress of the material. Thus, iron with $1/B = 120$ is brittle in tension in liquid air; a coarse grained pearlitic steel with $1/B = 200$ is substantially brittle at $-180^{\circ}C$, but for steels with tempered martensite structures $1/B = 500$, and they are ductile at this low temperature. The converse is of course true, and from the value of $1/B$, and the ductility at some low temperature, some estimate of the transition temperature in the notched bar test can be obtained.

In the case of a steel susceptible to temper brittleness, where $S_1$ is the brittle strength in the unembrittled state, and $S_2$ is the brittle strength after embrittlement, then the change in transition temperature in the impact test associated with this change in brittle strength is given by the expression:-

$$\frac{1}{B} \ell n. \left( \frac{S_1}{S_2} \right)$$

This means that the change in transition temperature as a measure of temper embrittlement does not represent any definite change in brittle strength, but depends

on the other mechanical properties of the steel. For example, 1/B is less for pearlitic steels than for tempered martensitic steels of the same composition, consequently the change in transition temperature for a given change in brittle strength will be less for the pearlitic steel. The lower susceptibility of pearlitic steels to temper brittleness has been demonstrated by Pellini and Queneau[22].

Referring again to equation (9), it is seen that for tempered martensitic steels, the tensile properties at normal or low temperatures are unlikely to be much affected by temper brittleness, unless severe embrittlement occurs such that the transition temperature in the notched bar test is raised above 200°C. Not until the transition temperature exceeds about 350°C can complete brittleness in tension in liquid air be expected to occur. Direct measurements of the brittle strength should therefore be possible in extreme cases of temper embrittlement. No experiments have been reported in the literature with this object in view, and no direct measurements of the brittle strengths of tempered martensitic alloy steels have been made. De Haas and Hadfield[52] who tested many steels in liquid hydrogen (-253°C), found that the ductility of a quenched and fully tempered nickel-chromium steel was considerably

reduced at the low temperature (the reduction in area fell from 60% to 49%). Annealed steels of this type were found to be more brittle at this temperature. At -180°C however, most heat treated low alloy steels showed very little reduction in ductility compared with the room temperature properties.

The main conclusions to be drawn from the discussion given above are:-

(1) Orowan's theory can be put into a mathematical form convenient for analysis of experimental results provided that a suitable expression is used to express the dependence of yield stress on temperature.

(2) The transition temperature in a notched bar impact test is a simple function of the brittle strength.

(3) Temper brittleness and the associated changes in transition temperature can be ascribed solely to changes in the brittle strength of the material; i.e. a decrease in cohesive strength without alteration of the yield strength.

(4) The change in transition temperature due to a given change in brittle strength depends solely on the effect of temperature on the yield stress of the material.

(5) The low temperature tensile properties of temper brittle steels should give a reliable guide to the extent of embrittlement, and in extreme cases the material

should be completely brittle at the temperature of liquid air. Pearlitic steels should show this effect more strongly than tempered martensitic steels.

# CHAPTER 3

## PRELIMINARY WORK.

This chapter contains an account of the preliminary work in the investigation, and includes a description of the manufacture of the steels, and of the apparatus used for heat treatment.

### Manufacture of Steels.

(a) Arsenic bearing steels. It was intended to use three types of steels to study the effect of arsenic on temper brittleness, corresponding to British Standards E.N.23, E.N.23 plus molybdenum, and E.N. 15. Each type of steel was to be made with four different arsenic contents, approximately 0%, 0.08%, 0.15% and 0.25%. The steels were made at Brown-Bayley's Steelworks Ltd., Sheffield, and the whole manufacturing process was carefully followed at the works.

An estimate was first made of the arsenic loss on addition to a melt. A small packet of arsenic was added to a part of a high frequency furnace melt, and the arsenic content was determined after casting. This experiment showed that considerable loss of arsenic occurred whilst it was dissolving in the melt, even though the packet was completely immersed in the molten

metal. It appeared that most of the losses occurred because of the sublimation of the arsenic at the time of the immersion. After about thirty seconds, the white fumes which were given off, subsided, and it was presumed that solution was complete; further losses appeared to be small. A figure of thirty-five per cent. was eventually arrived at for the loss of arsenic during solution.

The procedure adopted was as follows:-
when a melt was ready for pouring, the first ingot was teemed, to give the "arsenic free" steel. The first addition of arsenic was then made to the melt by plunging a packet containing the appropriate amount into the molten metal. The packet, (the arsenic, in a small envelope, was wrapped up in mild steel sheet) was attached to a steel rod, and could be held under the surface of the metal, thus preventing large sublimation losses. Solution was soon complete, and the second ingot was immediately teemed. The second and third additions of arsenic were then made in a similar way, and in each case, teeming was carried out as soon as possible after solution was complete. Each of the three melts was about four cwts., made from Armco iron, nickel-chrome and medium carbon steel scrap, with additions of ferro alloys etc., as required, to adjust the values of the

alloying elements. The melting was carried out in a small high frequency furnace (600 lbs. capacity). The melting time was about sixty minutes, and the total time including pouring was about ninety minutes for each melt.

The metal was teemed at a temperature in the range 1570-1590°C, except for the final ingot of the E.N. 15. (In this case the pouring temperature was somewhat lower, and the ingot mould was not completely filled.) The ingot moulds used were of four inches square section, top poured through a 7/8ths inch tundish, and hot tops were used to ensure maximum freedom from pipe and associated segregations in the main body of the ingot.

The average weight of each ingot was about 105 lbs., and no unusual difficulties were encountered in the production of them (except for the one mould which was not completely filled).

The ingots were next hammer cogged in two stages, over the temperature range 1040-900°C, down to about 2½ inches square billets. After surface grinding, these billets were cogged down to 1½ inch rounds, in six passes; the starting temperature being about 1000°C. These rods were then cut into three, reheated to 1030°C, and were then rolled down further, the last pass being

taken at about 860°C, to give round rods of about 0.55 inches diameter. No difficulties due to hot shortness were experienced in any of the hot working processes, and there was no evidence of any adverse effects due to the arsenic.

The rods were then hardened in oil from 850°C and tempered at 650°C, and finally ground to 0.45 inch rods, suitable for making into Izod specimens.

The works analysis of the steels are given in Table II overleaf. (casts numbered 2244-2246).

The arsenic contents of the "arsenic free" steels are seen to vary somewhat, and in general they are rather high. It is apparent therefore, that it could be variations in the arsenic content that lead to apparently random variations in the impact properties of steels. The high value of the arsenic in the E.N. 15, is probably due to the high percentage of the medium carbon scrap used in the charge.

(b) Antimony bearing steels. Steels containing Antimony were made to British Standard EN 23, and EN 23 plus Molybdenum, with 0% and 0.08% antimony. The method of manufacture was similar to that used for the arsenic bearing steels, except that only four ingots were made (two of each type), and that all were made from the same melt. In this case, the antimony losses

## Table II

| I.L. | Cast No. | B.S. EN No. | C | Si | Mn | S | P | Cr | Ni | Mo | As | Sb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| O | 2244/1 | EN 15 | 0.37 | 0.26 | 1.95 | 0.041 | 0.035 | 0.11 | 0.10 | - | 0.032 | - |
| P | /2 | " | 0.37 | " | 2.00 | " | " | " | " | - | 0.086 | - |
| Q | /3 | " | 0.38 | " | 1.95 | " | " | " | " | - | 0.15 | - |
| R | /4 | " | 0.38 | " | 2.00 | " | " | " | " | - | 0.25 | - |
| S | 2245/1 | EN 23 | 0.38 | 0.20 | 0.43 | 0.029 | 0·024 | 0.66 | 3.01 | 0.05 | 0.021 | 0.005 |
| T | /2 | " | 0.41 | " | " | " | " | " | 3.02 | " | 0.085 | - |
| U | /3 | " | 0.42 | " | " | " | " | " | 3.00 | " | 0.145 | - |
| V | /4 | " | 0.40 | " | " | " | " | " | 3.01 | " | 0.253 | - |
| W | 2246/1 | EN23+ Mo | 0.42 | 0.18 | 0.46 | 0.029 | 0.023 | 0.66 | 3.02 | 0.59 | 0.019 | - |
| X | /2 | " | 0.41 | " | " | " | " | " | 3.03 | " | 0.087 | - |
| Y | /3 | " | 0.41 | " | " | " | " | " | 3.02 | " | 0.15 | - |
| Z | /4 | " | 0.40 | " | " | " | " | " | 3.02 | " | 0.23 | - |
| A | 2892 /1 | EN 23 | 0.42 | 0.16 | 0.27 | 0.028 | 0.032 | 0.81 | 3.04 | 0.05 | - | 0.005 |
| B | /2 | " | 0.40 | 0.18 | 0.26 | 0.025 | " | 0.79 | " | 0.03 | - | 0.085 |
| C | /3 | EN23+ Mo | 0.41 | 0.17 | 0.23 | 0.029 | 0.030 | 0.78 | 3.05 | 0.50 | - | 0.007 |
| D | /4 | " | 0.41 | " | " | 0.038 | " | " | " | " | - | 0.088 |

% by Weight.

were greater than the arsenic, 50% of the element charged being lost. Of the four ingots, the EN 23 plus Sb was blown at the top, but the unsound part of the ingot was removed before hot working. The final heat treatment given this series of steels was:- oil hardened from 850°C, tempered at 640°C. The compositions are given in Table II. (Cast No. 2892).

Construction of Apparatus.

The initial decision to have the experimental steels rolled to the specimen diameter (0.45" diam.), was dependent on the use of suitable heat treating equipment to prevent oxidation of the material. Apparatus was constructed, both for hardening and tempering the steels in a neutral environment.

For the hardening treatment, a vertical tube furnace was used, which was continuously evacuated during the treatment, the general features of this furnace are shown in Figure (9). The silica tube was wound with about 8 turns per inch of 18 gauge Brightray wire, and with two subsidiary coils of 24 gauge wire at both ends to compensate for the end heat losses. About twenty bars of the correct size for making into two notched bar test pieces each, were supported in the furnace on a stainless steel place, which was itself

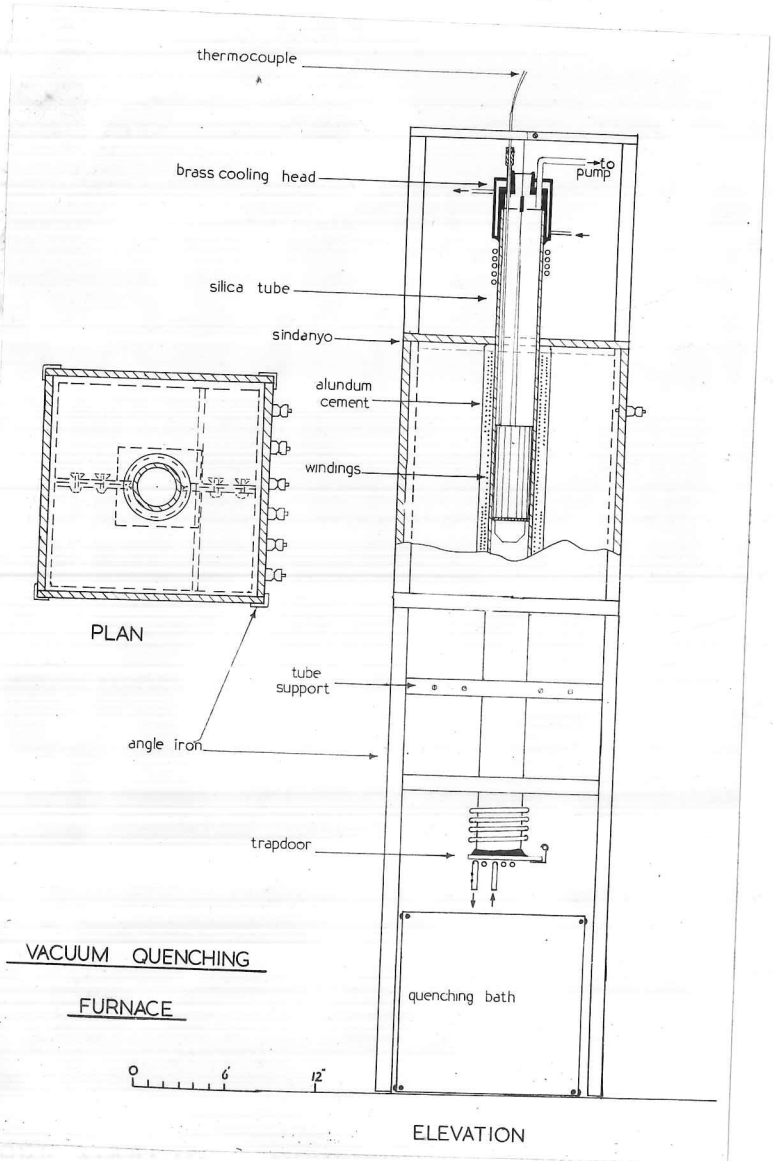
thermocouple
brass cooling head
to pump
silica tube
sindanyo
alundum cement
windings
PLAN
tube support
angle iron
trapdoor
quenching bath
VACUUM QUENCHING FURNACE
0
6"
12"
ELEVATION

Fig. 9

suspended on two tungsten wires (0.9 mms. diam.). In the cooling head, the tungsten wires are connected to a short length of Brightray, which is brought out of the vacuum through a picein seal, and attached to a cross bar above the furnace. When this wire was released (by severing it), the specimens fell down the tube, broke open the hinged plate at the lower end, and then fell directly into the oil quenching bath. The hinged plate was sealed with picein wax, which enabled the vacuum to be maintained until the moment of quenching. The furnace was evacuated with a two stage rotary pump (20 litres/sec.), and when the apparatus was cold a vacuum better than five microns was easily obtained. The pressure in the furnace during heat treatment usually increased to a maximum of about forty microns, attained when the maximum temperature was reached; after this, when the temperature was constant, the pressure dropped slowly. The specimens, after quenching were quite free from scale, although a very thin oxide film had formed. No appreciable alteration in diameter had taken place. The usual working temperature of the furnace was 900°C, but the maximum possible temperature was about 1000°C. Control of temperature was effected with Sunvic energy regulators, on both main and subsidiary coils. The temperature of heat treatment was maintained

to within 2°C of the desired temperature. This accuracy, attained with simple controllers of the Sunvic type, probably depended on the large thermal capacity of the furnace insulation. Temperatures were measured with a Chromel-Alumel thermocouple and a milivoltmeter, calibrated at standard temperatures.

For tempering and embrittling, two salt bath furnaces were constructed. One of these was for the range 300°C to 550°C, and the other for the range 550°C to 700°C. The salt pots were made of Chronite metal, and were of sufficient capacity (300 cu.inches) to ensure that the introduction of twenty cold specimens into the molten salt did not lower the bath temperature by more than about 20°C. By judicious overheating of the salt before immersing the material to be heat treated, it was found possible to attain the heat treating temperature about 6-8 mins. after the specimens had been put in. The pots (flat bottomed) were heated with hot plates (the type used in electric cookers), and by subsidiary windings at the sides of the pot. These windings ensured that the melting of the salt proceeded initially from the sides of the pot, and thus prevented any danger from the pressures set up due to the thermal expansion of the salt on melting. Temperature

control was effected by Sunvic energy regulators on both the hot plate and the subsidiary coil. These enabled the temperature to be maintained constant to within 3°C, provided the apparatus was given periodic supervision. For long treatments there was some drift, so that the overall accuracy was probably no better than 5°C. The temperatures of the baths were measured with a Chromel-Alumel thermocouple, and were recorded on a thread recorder. The salts used were I.C.I. Ltd. products; C.Q. 530 for the higher range, and T.S. 220 for the lower range. In the heat treatments used, very slight pitting was the only evidence of any attack by the salts on the EN 23 steels, but considerable amounts of non-adherent film formed on the EN 15 steel in the T.S. 220 bath. In this case the diameter was reduced slightly.

When very long tempering times were required, the salt pot was heated in a forced air circulation furnace.

For certain experiments, where high austenising temperatures were used, an EFCO resistance heated salt bath was used, (in the range 1150-1350°C). Although preventing serious attack, the salt bath was liable to develop considerable temperature gradients, resulting

in non-uniform grain sizes.

In certain very long embrittling treatments, (up to 1000 hours) which were used for a few tensile specimens, a small tube furnace, with high thermal capacity were used, and was controlled by a Cambridge Indicator-Controller ($\pm$ 2°C).

# CHAPTER IV

## THE EFFECT OF ARSENIC AND ANTIMONY ON TEMPER BRITTLENESS

### Heat Treatment.

In the determination of the susceptibility of steels to temper brittleness by measuring the displacement of the transition temperature it was decided to adopt the method of Jolivet and Vidal[17] in which isothermal treatments are used, both for the initial tempering and the embrittling treatment. This is probably more satisfactory than using slow cooling after tempering, and is easier experimentally. The heat treatments used are listed in Table III below:-

Table III

| Steel | Hardening | Tempering | Embrittling |
|---|---|---|---|
| EN 15 | 900 | 620 | 525 |
| EN 23 | 900 | 620 | 525 |
| EN 23 + Mo | 900 | 650 | 525 |

All temperatures in degrees Celsius.

In the hardening treatment, the specimen blanks were treated in batches of forty, twenty specimens being used to determine one transition curve. The

blanks were heated to 900°C in about two hours, and were maintained at temperature for one hour, followed by oil quenching. The tempering temperatures were selected in order to give a hardness of about 300 Vickers for the EN 23 steels, and about 250 Vickers for the EN 15 steel. In all cases the tempering time was two hours. The heating time in this case was about eight minutes. The embrittling temperature was selected to be 525°C, as this has been considered by most investigators to be the temperature of maximum rate of embrittlement. At this temperature the rate of embrittlement appears to fall rapidly after about one hour, and at times greater than four hours, the reaction proceeds quite slowly. Thus by taking the embrittling time as four hours, it was hoped to eliminate effects of rate of embrittlement, and to measure the maximum amount of embrittlement possible at 525°C. In certain cases, further tests on specimens treated for eight hours at 525°C confirmed that the embrittlement was only slightly increased by the extra four hours, and two series of tests on coarse grained steels in which 250 hour treatments were used, further confirmed this.

After heat treatment, the specimen blanks were machined, to cut the notch and the flat at the end. A special jig was used for this, cutting both the notch

and the flat on four specimens at the same time. The dimensions were those specified by the British Standards Institution.

Testing.

The actual testing was carried out on a standard 120 foot pound Izod machine, with a striking velocity of ft./sec. In tests over a range of temperature, the conduction of heat from or to the anvil of the machine must be considered. After a little practice it was found possible to break a specimen within one second of tightening the anvil on it. The effect of conduction on the temperature distribution of a cooled specimen is to raise the temperature of the peripheral zone, and if a rise of temperature of 2°C is considered, then it is apparent that the zone in which this rise in temperature takes place, moves inwards to the centre of the specimen. However, for a specimen initially at -140°C, the time taken for a 2°C rise in temperature to be transmitted to the centre was found to be 4 seconds, at the level of the notch (as measured by a thermo-couple). At the time of fracture, (after one second) the zone of increased temperature extends only a small distance from the surface (circa 1/16") and the base of the notch is still at the nominal temperature of the

specimen. Thus, the conduction does not affect the temperature (as measured initially) at which the transition from tough to brittle failure takes place; it only affects the energy absorbed in the case where brittle fracture has propogated across most of the specimen, and reaches the peripheral zone where the temperature is raised. Here, ductile failure takes place which would not otherwise have done so. It is seen therefore that the conduction of heat from the anvil does not materially affect the maximum impact value, or the transition temperature, but only the minimum value reached.

This was confirmed experimentally by constructing grips, in which the surfaces clamping the specimens were made of thermally insulating material (Tufnol). In this case the temperature as measured at the centre of the specimen of a bar initially at -120°C, did not rise until after 8 seconds, and at a point 0.05" from the centre until after 4 seconds. In this case it is immediately obvious that the effects due to conduction of heat from the anvil can be neglected. Fig. 10 shows the results of two series of tests on the steel S (EN 23), in the as received condition. The difference in the transition temperature between the insulated and the non-insulated grips is clearly quite small, and on the criterion used, it is about 3°C; this is probably

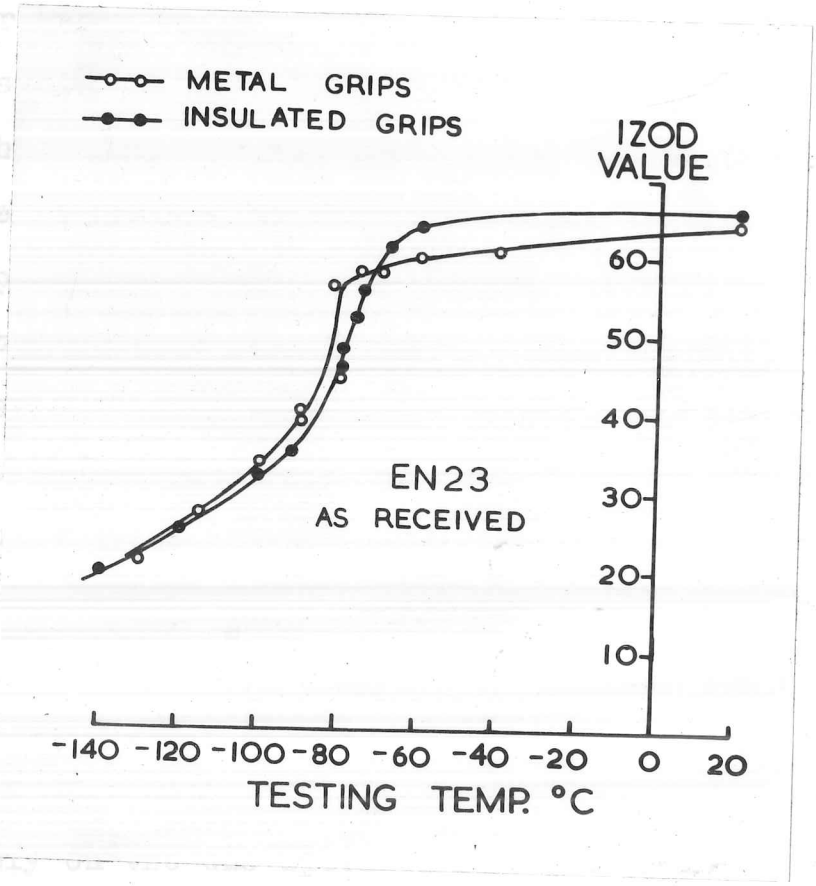
METAL GRIPS
INSULATED GRIPS
IZOD VALUE
60
50
40
30
20
10
EN23
AS RECEIVED
-140 -120 -100 -80 -60 -40 -20 0 20
TESTING TEMP. °C

Fig. 10

within the experimental error of the determination. It was necessary to limit the use of the insulated grips, as the tufnol tended to disintegrate after much use, and so they were only used at the extremes of temperature (outside the range -100 to + 100°C). Otherwise, the standard grips, lined with vaseline were used.

In this work the transition temperature was taken as that temperature at which the energy absorbed is reduced to 75% of the maximum impact value. Other possible criteria used by recent authors are (1) the highest temperature at which any trace of brittle fracture is present in the broken specimen, and (2) the temperature at which the impact value is reduced to 50% of the maximum impact value. Criterion (1) which appears attractive at first sight, is open to two objections:- (a) the transition temperature is measured by plotting % Brittle fracture v Temperature; the measurement of the relative areas of the brittle and ductile failure is difficult to perform with accuracy due to the irregularity of the surface. (b) The measured value of transition temperature depends ultimately on the one specimen with the least amount of brittle fracture present; further more, the greatest spread in the test results seems to occur at just the temperature it is desired to measure.

Criterion (2) overcomes these difficulties, but is then not easily comparable with tests using criterion (1). It is thought that a better average value for the series of specimens is obtained by taking the energy criterion rather than the fracture criterion, and also that the energy criterion is more objective. In order to make it more comparable with the latter, which has the merit that it is probably more significant from a theoretical viewpoint, it was decided to use a twenty-five percent energy drop as the criterion for the present work. This discussion is only relevant in those cases where the slope of the transition curve is gradual, and there are considerable differences between the temperatures obtained with the different criteria. For steep transition curves the differences tend to zero. It can also be noted here that with the temperature given by criterion (1) the energy has already fallen by a small amount (about 18% in some cases). What factors control this small drop are not known, nor is it clear whether there is any significance in it.

There seems to be little to choose between these three ways of measuring transition temperature, in so far as semi-quantitative results are concerned.

In the actual testing, it was necessary to be able to cool or heat the specimens to any temperature in

the range -160 to 350°C. For specimens above room temperature, heating was effected with oil or water baths. For testing below room temperature, a specimen was placed in a closely fitting thick-walled aluminium cylinder. The whole was then cooled to slightly below the required temperature with solid carbon dioxide, or liquid air. The cylinder was then suspended in a Dewar flask, in which thermal equilibrium was attained, and the metal gradually warmed up at a rate of ½-¾°C per minute. (For the lower temperatures it was found useful to have about 5 c.c. of liquid air in the bottom of the flask.) When the desired temperature was reached, the specimen was removed from the containing cylinder, and tested immediately. Temperatures were measured with a Chromel-Alumel thermo-couple inserted in a suitable hole in the block, so that the thermo-junction was close to the notch in the specimen.

Impact Properties of Steels Containing Arsenic.

For all the steels containing arsenic the hardening treatment developed an austenitic grain size of about 8 (A.S.T.M scale), and the hardenability was quite sufficient to ensure the transformation of the specimen to 100% martensite. It was found however, that the centre of the specimen was usually ten points lower in hardness (V.P.N.). The tempering produced a uniform sorbitic structure, and Fig. 11 shows the structure of EN.23 (S),

Fig. 11 x 1000

etched in nital, which is typical of all the steels in this series.

The Izod Value - Testing Temperature curves were determined for the EN 23 and the EN 23 + Mo steels for zero embrittling time, and after four and eight hours at 525°C, and these curves are shown in Figures A1 to A4*. The transition temperatures are recorded in Table IV, together with the hardness of the test pieces at the various stages of the heat treatment, the austenitic grain size (A.S.T.M.), and certain observations on the fractures of the specimens which will be referred to in a later chapter.

Referring to the EN 23 steel, it is apparent that as the amount of arsenic increases, the transition temperature increases in both the tough and brittle states, and that the displacement of the tough curve due to the treatment at 525°C also increases with increasing arsenic content. This is shown clearly in Fig (12), where the curve Ta refers to the steels after tempering at 625°C 'tough', and Tb to the steel after embrittling at 525°C for 4 hours. $\Delta T$ is the numerical difference (Ta-Tb). This notation is used in other figures.

It is also evident that although the arsenic increases the susceptibility to temper brittleness, the

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* All transition curves are given in the appendix A, at the end of the volume, and these figures are indicated by the prefix A.

Table IV

| Designation (EN23) | Vickers Hardness | | Grain Size | Transition Temperature | M.I.V. | Fracture |
|---|---|---|---|---|---|---|
| | O.Q. | As tested | | | | |
| S | 609 | 284 | 8-9 | -112 | 65 | Cleavage |
| SB | " | 281 | " | -42 | 65 | Intergranular |
| SB8 | " | 280 | " | -25 | 68 | Intergranular |
| T | 610 | 282 | 8 | -98 | 65 | Cleavage |
| TB | " | 280 | " | -28 | 63 | Intergranular |
| TB8 | " | 284 | " | -12 | 66 | Intergranular |
| U | 604 | 288 | 8 | -94 | 66 | Cleavage |
| UB | " | 284 | " | +4 | 65 | Intergranular |
| UB8 | " | 284 | " | +12 | 69 | Intergranular |
| V | 596 | 291 | 7-8 | -78 | 66 | Mostly cleavage |
| VB | " | 289 | " | +46 | 64 | Intergranular |
| VB8 | " | 284 | " | +50 | 69 | Intergranular |

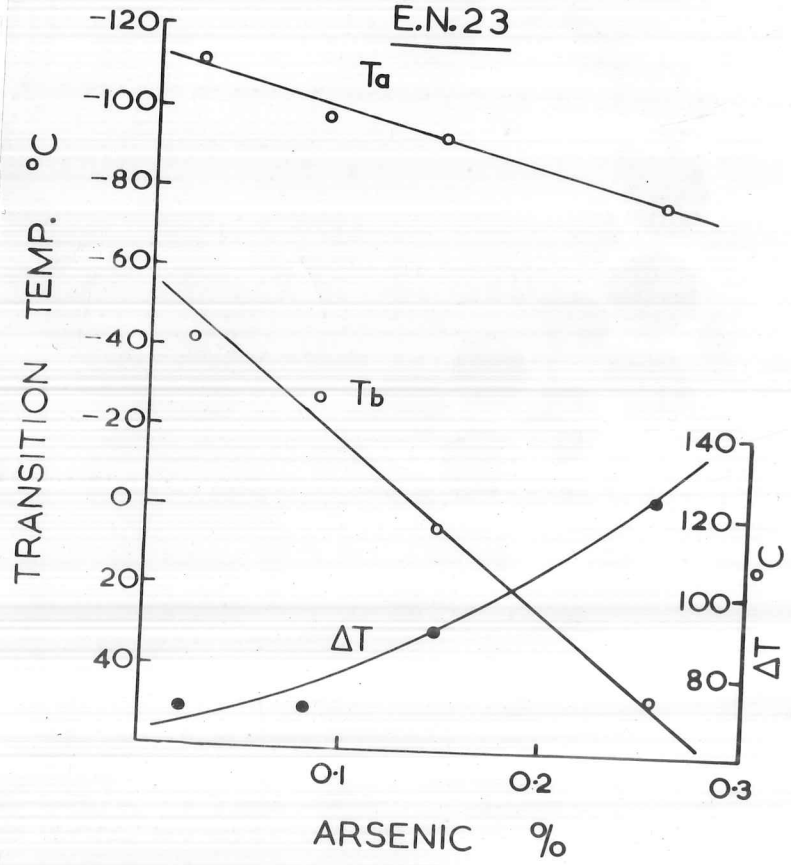

E.N.23
Ta
Tb
ΔT
TRANSITION TEMP. °C
-120
-100
-80
-60
-40
-20
0
20
40
140
120
100
80
ΔT °C
0·1
0·2
0·3
ARSENIC %

Fig. 12

steel is still very susceptible at the lowest value of the arsenic concentration (0.021%). Increasing the arsenic by a factor of ten, nearly doubles the displacement of the transition temperature. Referring again to Table IV, a comparison of the transition temperatures at 4 and 8 hours embrittlement indicates that the rate of embrittlement in the period 4-8 hours is quite small, and also that there is a definite tendency for the change in transition temperature due to the extra embrittlement to be less in the steels containing higher arsenic. This implies that the higher susceptibility of these steels is only apparent because of the higher rate of embrittlement and not because of the greater amount at equilibrium.

With the EN 23 + Mo steels (Table V and Fig. 13) the effect of the arsenic is very marked, since these steels show practically no susceptibility at the lowest arsenic content. The total magnitude of the increase in displacement (34°C) as between the steels containing the highest and lowest amounts of arsenic, is about half that in the molybdenum free steels. It appears therefore that in the most unfavourable conditions, molybdenum only reduces the susceptibility of EN 23 steels to temper brittleness, and does not suppress it entirely. Again in this case, the transition temperatures of the steels given the 8 hour treatment show that the rate of embrittlement

Table V

| Designation (EN23+Mo | Vickers Hardness | | Grain Size | Transition Temperature | M.I.V. | Fracture |
|---|---|---|---|---|---|---|
| | O.Q. | As Tested | | | | |
| W | 627 | 317 | 8-9 | -126 | 53 | Cleavage |
| WB | " | 313 | " | -116 | 53 | Cleavage with some Intergranular |
| WB8 | " | 306 | " | -106 | 58 | Cleavage and Intergranular |
| X | 635 | 316 | 8 | -124 | 53 | Cleavage |
| XB | " | 318 | " | -102 | 53 | Cleavage and Intergranular |
| XB8 | " | 301 | " | -98 | 59 | " " " |
| Y | 628 | 316 | 8 | -118 | 54 | Cleavage |
| YB | " | 313 | " | -96 | 54 | Mostly Intergranular |
| YB8 | " | 305 | " | -90 | 56 | " " |
| Z | 621 | 318 | 8 | -114 | 51 | Cleavage |
| ZB | " | 316 | " | -70 | 50 | Mostly Intergranular |
| ZB8 | " | 303 | " | -76 | 56 | " " |

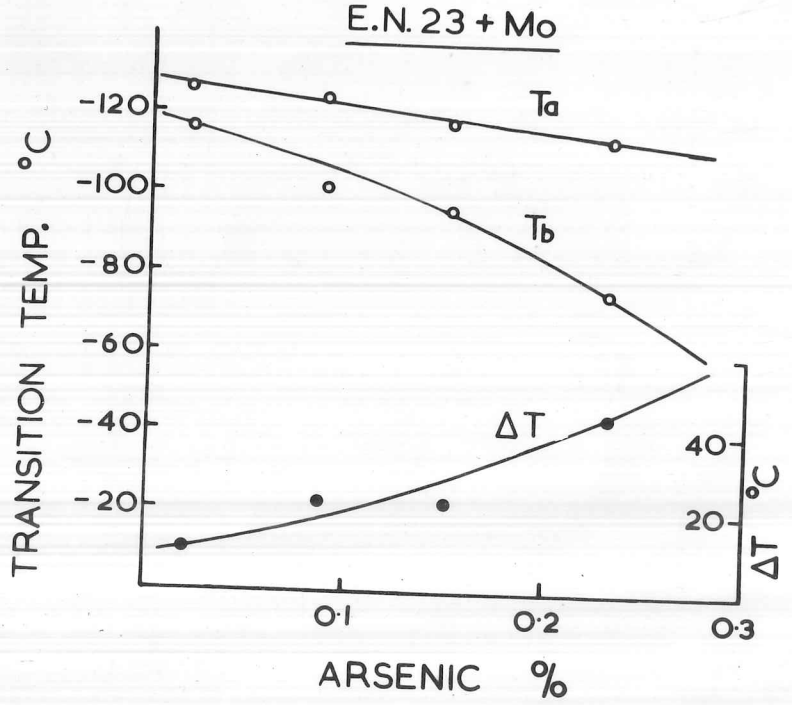

E.N. 23 + Mo
Ta
Tb
ΔT
TRANSITION TEMP. °C
-120
-100
-80
-60
-40
-20
40
20
ΔT °C
0·1
0·2
0·3
ARSENIC %

Fig. 13

after 4 hours is small, and that there is the same tendency for the change in transition temperature due to the extra 4 hours to be less for the steels containing the highest amounts of arsenic.

For both types of steels it can be concluded that:-

(1) Arsenic increases the transition temperature of tempered martensite even in the absence of temper brittleness.

(2) Arsenic increases the temper brittleness of tempered martensite.

(3) Molybdenum reduces, but does not suppress the temper brittleness, the retained susceptibility is in proportion to the susceptibility of the molybdenum free steel.

(4) There is some evidence to support the hypothesis that arsenic increases the rate of embrittlement rather than the maximum embrittlement attainable in a given steel.

Conclusions 1-3 are almost precisely the same as those reached by Bayertz, Craig and Sheenan[26][27], with respect to phosphorus. They studied the effect of variations of phosphorus content, and of additions of molybdenum, on the transition temperatures of low chromium and low manganese steels (SAE 5140 and SAE 1340). For the chromium steels the phosphorus was varied in the range 0.02% to 0.04%, and the molybdenum in the range 0% to 0.18%. The important difference between the two sets of results is

that the effect of the arsenic appears to be much less than that of phosphorus, both in respect to temper brittleness, and the transition temperature of the non-embrittled steel.

The conclusions of Bayertz et alia for the SAE 1340 steels are similar to those for the chromium steel, but they also stress the importance of the relative values of the molybdenum and phosphorus contents of the steels as a criterion for the amount of temper embrittlement.

From conclusion (1) it can be deduced that the effect of the arsenic on the 'tough' steel is to lower the brittle strength, because the room temperature tensile properties are not affected. As the low temperature fractures of the 'tough' steels were all substantially cleavage, the effect must be a solid solution one similar to that of nickel, but of opposite sign.

The results obtained with the manganese steels, Figs. A5 and A6, and Table VI, show considerable scatter. This was found to be due to the presence of large quenching cracks in the specimens. These had the effect of increasing the energy absorbtion above that for a sound specimen, in the transition range. Furthermore, in the steel containing the highest arsenic, pronounced segregation had taken place, so that the centre of the specimen

Table VI

| Designation (EN 15) | Vickers Hardness | | Grain Size | Transition Temperature | M.I.V. |
|---|---|---|---|---|---|
| | O.Q. | As Tested | | | |
| O | 570 | 254 | 7-8 | -80 | 84 |
| OB | " | 253 | " | +53 | 80 |
| P | 568 | 257 | 7-8 | -70 | 88 |
| PB | " | 255 | " | +62 | 79 |
| Q | 571 | 257 | 7-8 | -50 | 86 |
| QB | " | 256 | " | +92 | 79 |
| R | 560 | 254 | 7 | -68 | (96) |
| RB | " | 254 | " | +86 | 85 |

Transition Temperature in $^{o}C$.

when fractured, was found to be discoloured. Examination of the steel in the as received condition showed that the quenching cracks were present to some extent. In view of this, it was decided to discontinue experiments on this steel. However, from the results obtained, the general conclusion, that arsenic increases the transition temperature of the steel, in both 'tough' and 'brittle' steel can be made, and there is a tendency to increased temper brittleness.

It seems likely that the cause of the trouble in these steels is the combined effect of the high carbon and manganese contents.

It is to be noted that for all the steels the maximum impact value (M.I.V.) is more or less unaltered by the 4 hour treatment at 525°C, indicating that the normal tensile properties are not altered by the embrittlement (see below). After 8 hours, the maximum impact value is slightly higher, due to further softening.

One further effect of arsenic is apparent in the austenitic grain size. Arsenic appears to coarsen the grain slightly.

Tensile Properties of Steels Containing Arsenic.

The tensile properties of the EN 23 and EN 23 + Mo steels, for 0 and 4 hours embrittlement were determined on a standard Tensometer testing machine. The specimens

used were 0.1785" diameter (1/40 sq.in. cross section), with a gauge length of 0.632" (l = 3.54d). Using a 2 ton weigh bar, the accuracy of the values of stress were ± 2%, so that variations of 1 ton in the values are not significant. Tables VII and VIII give the following properties:- Yield Stress, Ultimate Tensile Strength, Fracture Strength (load divided by initial area), True Fracture Strength (load divided by area at fracture), % Reduction of Area, % Elongation, and also a brief description of the appearance of the fracture.

There appears to be no significant trend in any of the properties listed, although the steels containing the largest amounts of arsenic seem to have the U.T.S. about 1½ tons/sq.in. higher than the steels with lowest arsenic, and the stress at fracture appears to be increased slightly. It also is quite evident that there is no significant alteration in the properties due to the 4 hour embrittling treatment. The only feature of these tests which does show considerable variation is in the appearance of the fracture.

A prominent feature of the tensile fracture of many heat treated alloyed steels is the presence of cracks, radially distributed, but extending longitudinally along the specimen. This type of fracture is usually termed "star fracture". Associated with each crack is

Table VII

| Designation EN23 | Y.S. | U.T.S. | F.S. | T.F.S. | % Elong. | % R.of A. | Fracture |
|---|---|---|---|---|---|---|---|
| S | 48.4 | 55.6 | 36.8 | 105 | 24 | 65 | Some radial cracks |
| SB | 46.6 | 54.4 | 37.6 | 105 | 21.7 | 64 | Severe radial cracking |
| T | 47.2 | 54.4 | 37.6 | 109 | 25 | 65½ | As for S |
| TB | 45.2 | 55.6 | 38.0 | 110 | 26.5 | 65.5 | " " SB |
| U | 49.0 | 57.0 | 38.4 | 109.5 | 25.5 | 65 | " " S |
| UB | 48.8 | 56.8 | 38.4 | 109 | 24 | 65 | " " SB |
| V | 48.8 | 57.6 | 39.6 | 113 | 25.5 | 65 | " " S |
| VB | 48.0 | 56.8 | 38.4 | 109 | 26 | 65½ | " " SB |

Y.S. = Yield Stress; U.T.S. = Ultimate Tensile Strength; F.S. = Fracture Strength;

T.F.S. = True Fracture Strength; Elong. = Elongation; R.of A. = Reduction of Area.

All Stresses in tons/square inch

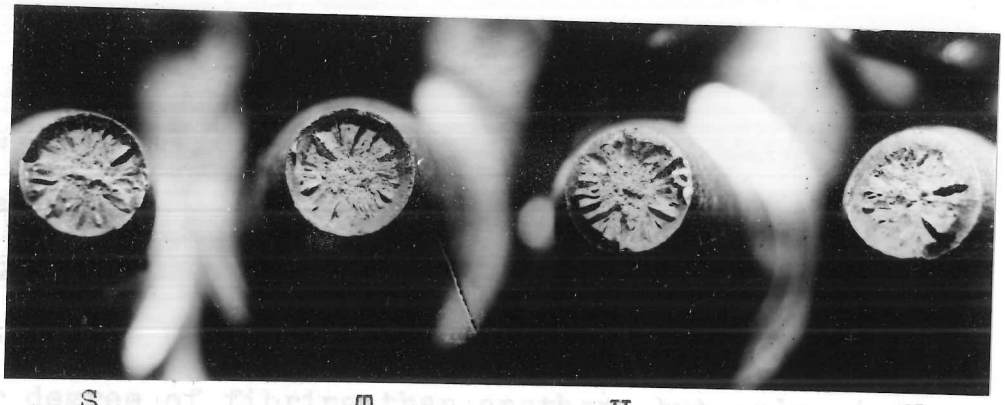
## Table VIII

| Designation | Y.S. | U.T.S. | F.S. | T.F.S. | % Elong. | % R.of A. | Fracture |
|---|---|---|---|---|---|---|---|
| W | 54.4 | 61.2 | 44.8 | 112 | 24 | 62 | Cup and cone |
| WB | 54.2 | 61.6 | 44.4 | 116.8 | | 62 | Slight radial cracking |
| X | 54.4 | 62.4 | 43.2 | 117 | 25 | 63 | " " " |
| XB | 56.8 | 64.0 | 46.4 | 116 | 24 | 61 | Marked " " |
| Y | 54.4 | 62.0 | 42.4 | 115 | 23 | 63 | " " " |
| YB | 54.4 | 62.0 | 45.6 | 114 | $24\frac{1}{2}$ | 60 | |
| Z | 55.2 | 62.4 | 46.4 | 116 | 24 | 62 | " " " |
| ZB | 54.4 | 62.4 | 45.6 | 114 | 24 | 62 | Severe " " |

Abbreviations as for table VII. All stresses in tons/square inch.

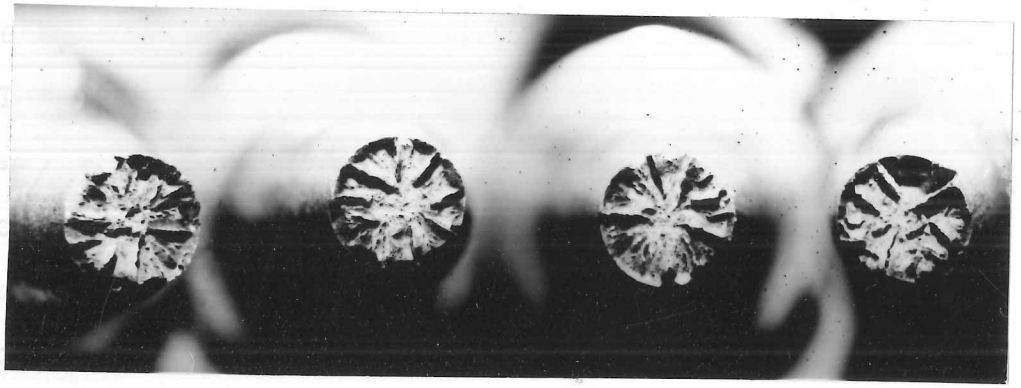
a small projection on either side (or indentation on the other side of the specimen) which may be termed ears. Hollomon[42] believes that this type of fracture occurs in temper brittle steels, and not in 'tough' steels, and reproduces the fractures of a manganese-molybdenum steel to support this view. Examination of the steels tested in this present work, indicate that this is not the general case. Fig. 14 shows the fractures of the specimens referred to in Tables VII and VIII. It is immediately evident that the presence or absence of the radial cracks does not give a reliable indication of the state of embrittlement of the material, but in general, they are more prominent in the embrittled steels. The EN 23 + Mo fractures show an effect similar to that described by Hollomon, but the presence of the star type fracture seems to depend more on the amount of arsenic present than on whether the steel has been embrittled. The cause of these cracks has been ascribed to a combination of (a) the fibre structure developed in the neck, causing a lowering of the transverse strength with respect to the longitudinal strength, and (b) the transverse stresses arising from the shape of the neck. It seems not unlikely however, that these cracks develop only whilst the main transverse crack is propagating. This main crack will give rise to much greater tangential stresses than those arising from

EN 23
'Tough'

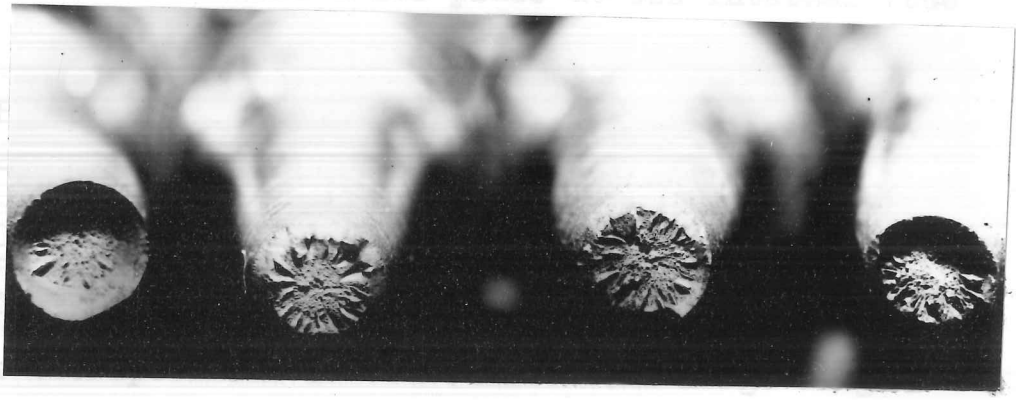


S T U V

EN 23
'Brittle



EN 23+Mo
'Tough'



W X Y Z

EN 23+Mo
'Brittle

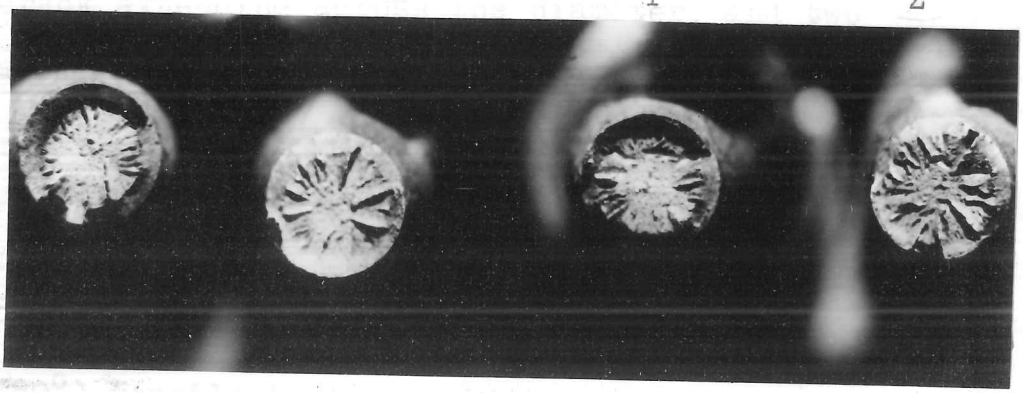


Fig. 14 x 6

the shape of the neck of the specimen. While it pro-propagates slowly across the specimen, there appears to be opportunity for the formation of the tangential cracks. This mechanism does not explain why one material shows a greater degree of fibring than another, but only gives a picture of the manner of failure.

The external surfaces of the ears referred to above, have the smooth appearance of the sides of the cup and cone part of the fracture, i.e. they seem to have been formed in shear. It is suggested that as the main transverse crack is propagating across a radial crack, the shear failure takes place at the internal free surface.

Hollomon also comments on the work of Lea and Arnold[12], who found that for a particular nickel-chrome steel on which they were experimenting, severe embrittlement produced a unique type of tensile failure. In this case the specimens fractured with one large longitudinal crack extending across the diameter, and two transverse cracks, one at each end of the longitudinal crack. This type of failure, seems to be related to the star fracture described above. It has not been observed on any of the specimens tested in this work, but Colbeck et alia[50] reported a similar failure in a low temperature ($-180^{\circ}$) tensile test on a high tensile steel of the

Vibrac type. As this steel contained 0.64% Mo, and was not given any special embrittling treatment, it seems unlikely that the longitudinal failure is related to temper brittleness, but is controlled by some other structural factor. A very similar type of fracture frequently occurs in hard drawn wolfram wire.

Impact Properties of Steels Containing Antimony.

The antimony steels were given similar heat treatments to those given to the arsenical steels. These are recorded in Table IX below:-

TABLE IX

| Steel | Hardening | Tempering | Embrittling |
|---|---|---|---|
| EN 23 | 900 | 620 | 525 |
| EN 23 Mo | 900 | 650 | 525 |

All temperatures in degrees Celsius.

The Izod Value-Temperature curves of these steel were determined for 0 and 4 hours embrittling time as previously. The transition curves are given in Figs. A7 and A8, and the transition temperatures are recorded in Table X.

The hardness of this series is greater than the arsenical steels, probably because of the increased chromium content. The slopes of the transition curves

Table X

| Designation | Vickers Hardness as | | Grain Size | Transition Temp. °C | | M.I.V. | Fracture |
|---|---|---|---|---|---|---|---|
| | O.Q. | Tested | | T | △ T | | |
| EN23 A | 625 | 303 | 8 | -100 | 62 | 52 | Cleavage |
| EN23 AB | " | 301 | " | -38 | | 51 | Intergranular |
| EN23 B | 623 | 306 | 7 | -24 | > 325 | 42 | Mostly Intergranular |
| EN23 BB | " | 305 | " | >+300 | | ? | Intergranular |
| EN23 C + Mo | 628 | 330 | 7-8 | -115 | 5 | 44 | Cleavage |
| EN23 CB + Mo | " | 331 | " | -110 | | 43 | Mostly Cleavage |
| EN23 D + Mo | 622 | 327 | 7 | -96 | 216 | 44 | Cleavage |
| EN23 DB + Mo | " | 327 | " | +120 | | 27 | Intergranular |

are more gradual for this reason, The maximum impact values are lower because of the greater hardness, and also because of the lower manganese content.

The increase in transition temperature for the EN 23 without antimony, corresponds closely with that for the steel S (Table IV). The addition of the antimony causes the unembrittled transition temperature to be raised by 76°C, and increases the displacement due to the embrittling treatment from 62°C to greater than 325°C. it was not possible to determine the transition curve for the embrittled antimony steel, as the transition was at so great a temperature. The antimony therefore, has an overwhelming influence on temper brittleness, as reported by Jolivet and Vidal(17).

For the EN 23 + Mo, a similar influence is shown. Antimony raises the transition in the 'tough' state by 20°C, and increases the displacement from 5°C to 216°C. This in effect means that although the molybdenum has reduced the temper brittleness,the steels are more susceptible with the added antimony, than the plain EN 23 steel without antimony. In this case the addition of molybdenum cannot be considered as a panacea for low impact values, where there is any likelihood of the presence of antimony in appreciable quantities. It can further be seen that (1) the maximum impact value is

reduced by the antimony, and (2) the embrittlement of the EN 23 + Mo steel has reduced the maximum impact value. These changes are reflected in the tensile properties.

The influence of the antimony on the transition temperature of the 'tough' EN 23 appears to be very great. This is not all due to the lowering of the brittle strength by a solid solution effect as in the case of the arsenical steels, because the brittle fracture of the antimony steel was mostly intergranular. This can mean either that these steels embrittle at 620°C, or that the embrittling effect due to the heating through the range 400-600°C was sufficient to embrittle the steel permanently. In the case of the EN 23 + Mo the low temperature fractures of the non-embrittled steels were both cleavage, and so the antimony definitely lowers the brittle strength in a manner comparable to that of arsenic. It may be concluded that:-

(1) Antimony raises the transition temperature of tempered martensite in the absence of temper brittleness.

(2) Antimony very greatly increases the temper brittleness of tempered martensite.

(3) Molybdenum reduces the temper brittleness womewhat, but still leaves the steel very susceptible.

Tensile Properties of Steels Containing Antimony.

The tensile properties of the antimony steels are

given in Table XI, and were determined in the same way as those for the arsenical steels. The same specimen size and testing machine were used. The table shows immediately that the effect of antimony is marked, both in the 'tough' and 'brittle' condition. The yield stress and the ultimate tensile strength are hardly affected, but the elongation and reduction of area are reduced, and the true fracture strength is lowered. The steel BB (EN 23 + Sb), shows only 17% reduction of area, and gave a flat intergranular fracture very soon after the maximum load was reached. This is the first really convincing evidence of the effect of temper brittleness on the room temperature tensile properties of alloy steels. It clearly implies that provided the embrittlement is sufficiently severe, the tensile properties are impaired. It is to be noted that there is no real strengthening effect or change in hardness, as might be expected if the phenomenon were a type of age hardening. There is a tendency for the yield stress to be slightly increased in the embrittled steels, but this effect is hardly greater than the experimental error.

The steels containing molybdenum show similar but less marked effects. In both cases the reduction of area correlates roughly with the maximum impact value.

Table XI

| Designation | Y.S. | U.T.S. | F.S. | T.F.S. | %Elong | %R.of A. | Fracture |
|---|---|---|---|---|---|---|---|
| EN23 A | 50.4 | 60.0 | 43.2 | 113.7 | 24 | 62 | C and C, with slight radial cracking. |
| AB | 51.4 | 60.3 | 43.1 | 115 | 24 | 62½ | Slight C and C, with well developed radial cracks. |
| B | 51.7 | 60.3 | 43.1 | 105.3 | 22 | 52 | C and C, with slight radial cracking. |
| BB | 52.3 | 60.7 | 59.9 | 72.3 | 10 | 17.2 | Intergranular --- flat transverse fracture. |
| EN23 + Mo C | 56.9 | 65.0 | 47.3 | 124.5 | 22 | 62 | C and C. |
| CB | 58.4 | 67.2 | 48.0 | 123.1 | 22 | 61 | C and C, with slight radial cracking. |
| D | 57.6 | 65.7 | 50.0 | 116.3 | 20 | 57 | C and C. |
| DB | 59.2 | 66.8 | 60 | 103.5 | 18 | 42 | C and C, with v. slight radial cracking. |

Abbreviations as for Table VII. All stresses in tons/square inch

The fractures of the tensile specimens show similar effects to those already mentioned for the arsenic bearing steels, but in this case the change of appearance due to the embrittling treatment appears to be more clearly marked. Taking these observations in conjunction with those given earlier, the following general observations can be made regarding the development of the star type fracture:-

(1) The composition and tempering treatment control the appearance of the fracture, and can give rise to either a cup and cone type fracture or a star type fracture. Molybdenum decreases, and arsenic increases the tendency of the star type fracture.

(2) For a steel which is temper brittle, there is a much greater tendency towards the star type failure, but this does not give positive proof of embrittlement.

Reversibility of Brittleness in Antimony Steels.

It has been tacitly assumed the antimony does produce a reversible, intergranular type of brittleness, i.e. that the phenomenon is temper brittleness. In order to ensure that the same reaction is taking place, it seemed desirable to check that the effect was reversible as far as the room temperature impact properties were concerned.

A series of specimens of the steel BB (EN 23 + Sb, 4 hours embrittlement) were heated in a salt bath at 620°C, for varying lengths of time, and then water quenched. The Izod impact values were then determined at room temperature, and are given in Table XII.

Table XII

| Time at 620°C (minutes) | Izod value (R.Temp.) |
|---|---|
| 0 | 2 |
| 5 | 4 |
| 10 | 5 |
| 20 | 13 |
| 40 | 30 |
| 80 | 27 |

Although a complete reversal of embrittlement was not obtained, the impact value is very much improved by the treatment at 620°C. The fact that after 80 minutes the impact value is only 27 (i.e. partly brittle) implies that some embrittlement does take place at 620°C. It becomes clear that this is the reason for the intergranular fracture of the tough steel B, referred to earlier. Further confirmation that the phenomenon is really temper

brittleness is recorded in a later chapter.

Conclusions.

(1) Both arsenic and antimony increase the transition temperatures of tempered martensite in the 'tough' condition.

(2) Arsenic slightly increases, and antimony greatly increases the tendency to temper brittleness.

(3) Arsenic does not affect the tensile properties of the steels studied, but antimony decreases the ductility, by an amount depending on the heat treatment.

(4) When embrittlement is sufficiently great, the tensile properties are impaired, and an intergranular fracture can result.

(5) The effects of antimony on the embrittlement are reversible, and have the definite characteristics of temper brittleness.

# CHAPTER V

## THE FRACTURE OF LOW ALLOY STEELS IN RELATION TO TEMPER BRITTLENESS.

### Introduction.

When metals fracture with little or no ductility, considerable information can be obtained about the internal structure of the metal by examination of the fractured surface. Fractures taking place with large deformations are much less discriminating and more difficult to interpret. The fractures of temper brittle steels, breaking with low energy absorption in room temperature impact tests have long been thought to be intergranular, and have been compared with the fibrous fracture of tough steels. For a comparison of the internal structure of 'tough' and 'brittle' steels by examination of the fracture, it is quite clear that both materials must be broken in such a way that both fracture without much deformation. A comparison of these fractures is most useful in supplementing the information concerning temper brittleness obtained from transition curves. This chapter gives an account of the examination of the low temperature impact fractures of the EN 23 steels in various heat treated conditions, and correlates this information with that recorded in Tables IV, V and X. The initial impetus for this type of work is due to Zapffe and Clogg (59),

McLean and Northcott[21] gave brief descriptions of the brittle fractures occurring in some low alloy steels.

Cleavage Fracture.

The phenomenon of cleavage is well known, and it is this type of fracture which usually occurs when mild steels fail in a brittle manner, due to stress concentration or low temperature. It is characterised by flat brightly reflecting surfaces (001 planes), which usually extend completely across the individual ferrite grains, and also by the geometrical markings on the surface (see ref. 58). In quenched and tempered steels, the ferrite grains are very small, and the fracture apparently loses the features typical of cleavage, appearing rather dull to the naked eye.

To investigate these fracture phenomenon, specimens of steel T(EN 23, 0.085% As) were oil quenched from 1250°C and tempered for one hour at 640°C. The high austenising temperature was used to develop a large austenite grain size, which made the subsequent observations much easier. The actual grain size established was rather mixed, but was in the range 0-3 (A.S.T.M. grain size). After being notched, a short bar of this material was fractured at -180°C, and the fracture examined at x 40 and x 400.

Examination of the fracture at x 40 showed that it was characterised by the sudden changes in direction of fracture at the austenite grain boundaries, each grain retaining its individuality. This is shown in Fig. 15. At a higher magnification the distinctive cleavage facets were visible (Fig. 16), the facets having 'feathery' shapes, as reported by McLean and Northcott. Many areas were observed with structures similar to that shown in Fig. 17, where a number of cleavage facets were found to lie in the same plane, and the spatial arrangement resembled the ordinary microstructure of the specimen. This seemed to indicate that the array of cleavage facets was in some way connected with the original martensite plates formed on quenching. It can further be noted that the individual facets were considerably larger than the known ferrite grain size (0.8$\mu$, or about 0.4 mms. on the figure). Fig. 18 shows the microstructure of the specimen after etching in an etheral solution of picric acid, containing 1% Cetyl-Trimethyl-Ammonium Bromide. (This reagent will be referred to as CTAB.) In this case the material was given an embrittling treatment at 525°C in order to ensure clear delineation of the austenite grain boundaries. The similarity between Figs. 17 and 18 is quite marked. In the fracture, the areas with cleavage facets in the same plane indicate that all the ferrite

Fig. 15 x 72 (Dark Field)

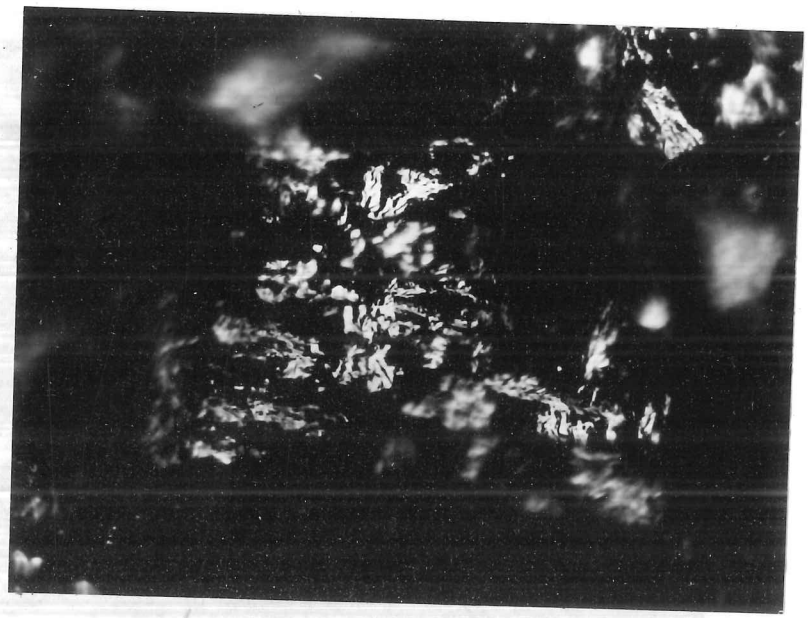


Fig. 16 x 420

Fig. 17 x 420

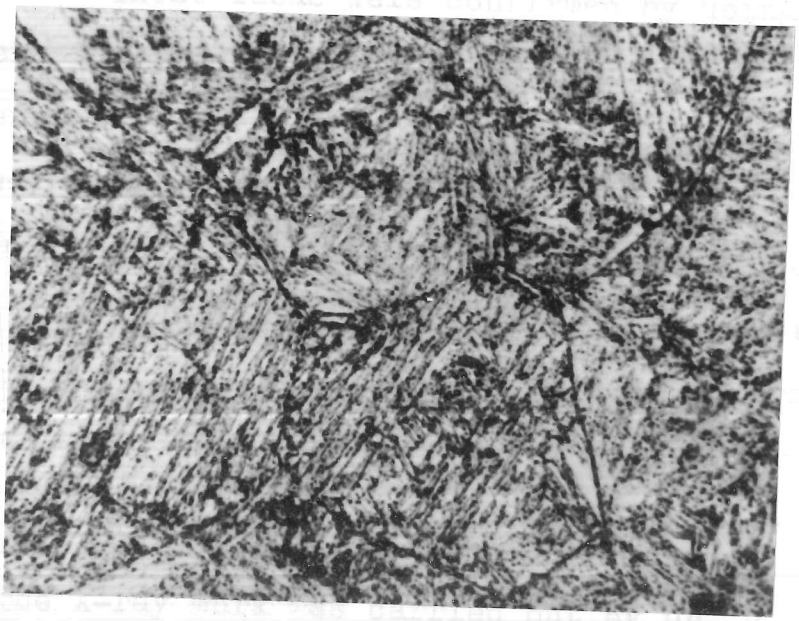


Fig. 18 x 420

grains over quite large regions had approximately the same orientation. Any one austenite grain is thought to transform to a limited number of regions in which the martensite orientation is uniform, with a small percentage of the area occupied by a more or less random array of martensite plates. (Actually only 24 orientations are possible, but where a large number of different orientations occur in a very limited region, this is considered random.) The plate structure is discernible in Fig. 18, and each grain appears to consist of about four areas of uniform orientation. Microstructures given by Carpenter and Robertson[60] for 0.1% carbon steels, show the same effect, but with much greater ordering. High carbon steels, show this type of phenomenon to a far lesser degree, as the habit plane of the martensite is different.

These ideas were confirmed by using an X-ray back reflection technique on a polished and etched specimen*. This type of photograph gave a spotty Debye-Scherrer ring. From the number of arcs, and the volume of material irradiated, it was possible to calculate the size of the regions of uniform orientation. The results obtained showed that the ferrite grains were assembled in aggregates of about 60$\mu$ diameter in which the grain orientation was substantially the same. The

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* The X-ray work was carried out by Dr. P.B. Hirsch, Cavendish Laboratory, Cambridge. The details are given in appendix B.

actual misalignments ranged up to 3° (this was obtained from the angular width of the arcs). As the mean equivalent austenite grain diameter was about 100μ, these results indicate that any one grain transforms to about eight orientations of martensite, and not to a random distribution of the 24 orientations as might be expected from the Kurdjumov-Sachs relationship. The microstructure and the fracture can therefore be correlated.

With fine grained steels, the fractures were more difficult to observe, but it was found that there was not such a marked tendency to the type of structure shown in Fig. 17. Each austenite grain appeared to transform to a smaller number of regions of preferred orientation than in the coarse grained steel.

This substructure of the tempered martensite can explain some of the characteristics of the impact properties of quenched and tempered steels. As the size the orientated regions depends on the austenite grain size, it is clear that the impact properties will also depend on the austenite grain size. The true ferrite grain diameter does not seem to depend very greatly on the austenite grain size, so this cannot be of importance in this case.

Hodge et alia[56] showed how the transition

temperature depended on the ferrite grain size of a low carbon, 3% nickel steel. When their value is extrapolated to 0.8$\mu$, the value obtained is -290°C. For a ferrite grain diameter of 60$\mu$, (the size of the orientated regions), the expected transition temperature is -105°C. The value of -290°C is unreasonable, but the value of -105°C is not very different from the estimated transition temperature for this steel (about -80°C), although some allowance must be made for the difference between the two impact tests used in the different cases.

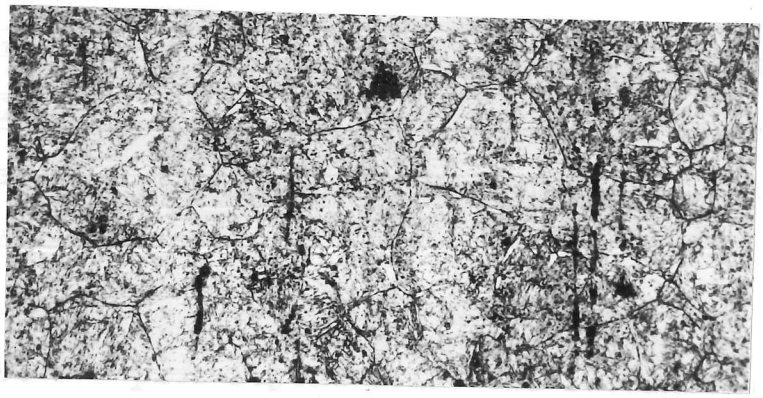
It is clear that unless the carbide particles in the tempered martensite exert a very large influence on the transition temperature, then it is the size of the ferrite aggregates of uniform orientation that is the controlling factor in determining the transition temperatures of quenched and tempered steels.

Intergranular Fracture.

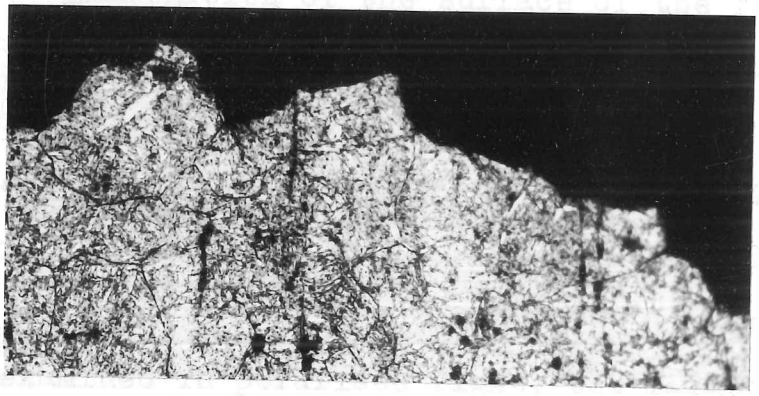
The fracture of temper embrittled steels was thought to be intergranular as long ago as 1919 (61), but there was considerable discussion, and opinion was not unanimous. One of the major difficulties, (that the austenite grain boundaries could not be satisfactorily delineated by metallographic techniques) was overcome by Cohen et alia[20] who developed the etching reagents

containing surface active chemicals. Using this reagent, it was found possible to demonstrate in a convincing way, that the fracture took place at the prior austenitic grain boundaries.

An Izod specimen (square section) of a severely embrittled coarse grained steel (T) was made in two halves. The plane of separation was along the longest axis of the specimen, perpendicular to the direction of impact. The two surfaces at the dividing plane were polished and etched with CTAB, to show up the austenite grain boundaries and then photographed. The two specimen halves were bolted tightly together, and the composite specimen was fractured at -180°C. In this way deformation at the polished surfaces was restricted. After fracture, the microstructure at the fractured edge was photographed and compared with the photographs taken previously. Plastic deformation had been almost eliminated, and it was possible to trace the course of the fracture across the specimen. It was found to be intergranular with respect to the prior austenite grains. Fig. 19a shows a typical area before fracture, and Fig. 19b the same area after fracture. Comparison of the two photographs shows the intergranular nature of the fracture. Portions of the edge that are slightly out of focus are regions where plastic deformation took place.



(a)



(b)

Fig. 19 x 150

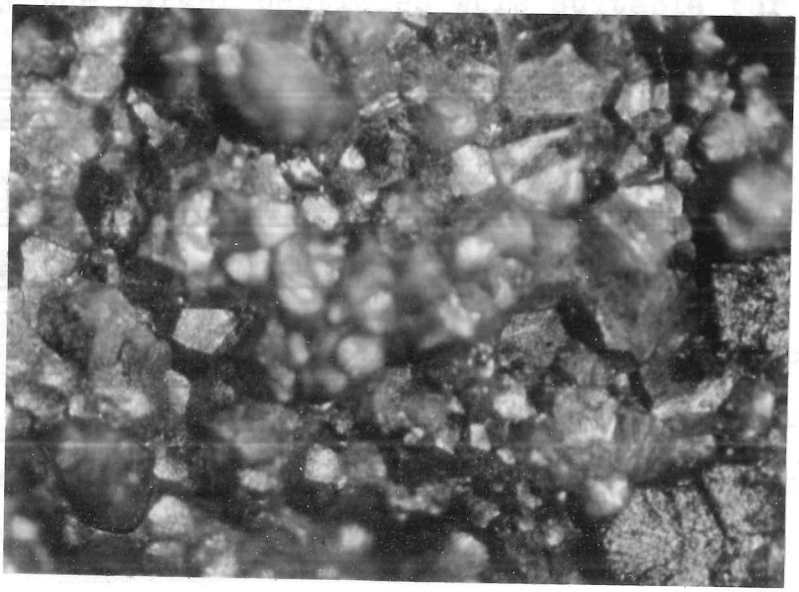


Fig. 20 x 72

The free surface was not favourable for propagating brittle fracture, and where grain boundaries were unfavourably orientated with respect to the advancing crack, some deformation has taken place before fracture. This evidence, together with that put forward by Nutting and Coslett[62] puts beyond doubt the intergranular nature of the fracture of temper brittle steels.

Examination of the surface of the fracture rather than the section showed the gently curved facets usually associated with intergranular failure (Fig. 20). The surfaces when examined at higher magnifications, (Fig. 21) appeared to be rough, and to contain very small particles, which were thought by Nutting and Coslett to be carbides. When examined in polarised light, the larger particles were found to have the same optical properties as the larger grain boundary particles in the microsection. Only the larger particles were suitable for observation. The grain boundary carbides were larger than average, which is consistent with the observation that the particles on the fractured surface were larger than average.

Mixed Fractures.

In general, the low temperature fractures of the low alloy steels examined were neither completely intergranular, nor completely cleavage. The steel T in the 'tough' condition contained some intergranular

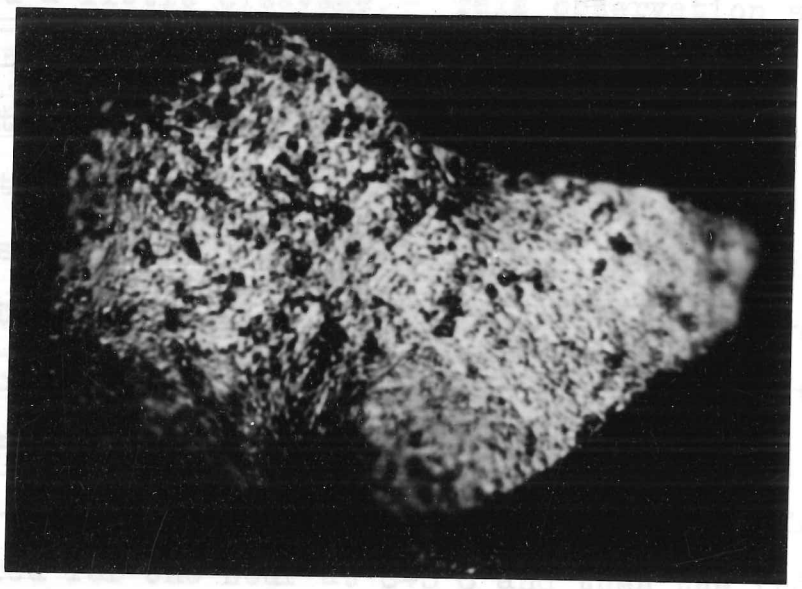
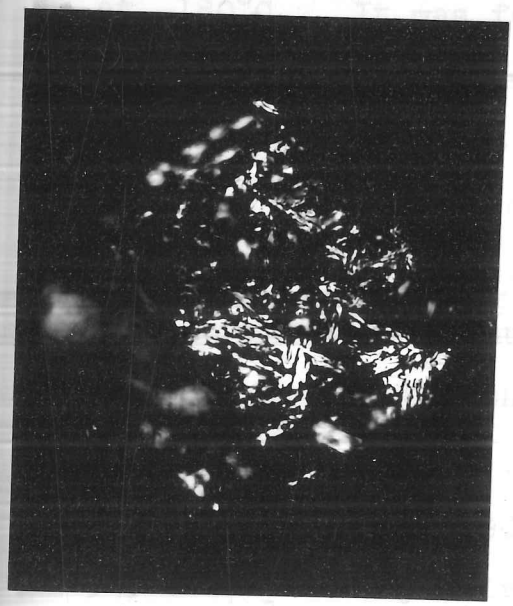
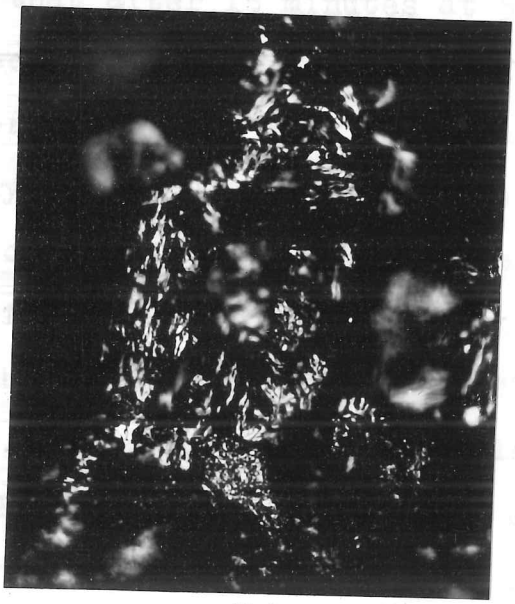


Fig. 21 x 840



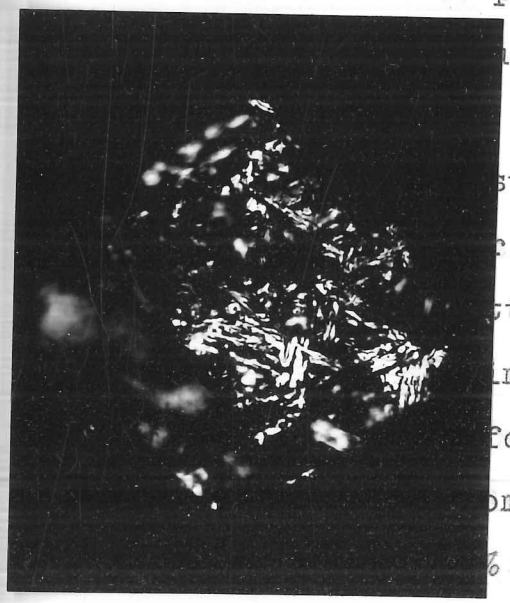
(a)



(b)

Fig. 22 x 430

facets, and when severely embrittled, the fracture contained a little cleavage. This observation suggests two enquiries:- (1) how does the change from cleavage to intergranular fracture take place with respect to the heat treatment? (a) does the presence of intergranular facets in the fractures of tough steels mean that the embrittlement takes place at temperatures above 600°C?



estion was dealt with in the follow-

steel T was oil hardened from 1250°C,
at 640°C and then the individual
tled for varying lengths of time
mens were then notched and fractured
found that after 15 minutes at 525°C,
me about 50% intergranular; after
% intergranular, and after 2 hours,
the fracture contained very little trace of cleavage facets. It thus becomes clear that the change from cleavage to intergranular fracture is rapid, but takes place in such a way that there is a continuous transition from one type to the other. The change in transition temperature associated with the 15 minute treatment at 525°C is probably only of the order of 20°C, and so it is evident that the examination of the low temperature fracture of steels can provide a sensitive criterion for

the presence of temper brittleness. This is of some industrial importance, since it provides a simple method of determining whether the most superior impact properties are being obtained in a given steel. Furthermore, if the assumption is made that the fundamental characteristic of temper brittleness is the intergranular fracture, and that temper embrittlement does not influence the cleavage strength, but only the intergranular brittle strength, then it follows that examination of the fracture can be used to discriminate between changes in transition temperature due to causes other than temper brittleness. Scarcely anything is known about the influence of elements in solid solution or as a separate phase on the cleavage strength of metals, but unless the precipitation actually takes place on the cleavage planes (in this case 001 planes) it seems unlikely that the cleavage strength will be altered. (From another point of view, temper brittleness can be defined in terms of the intergranular fracture, and then the rest follows.) It is certainly a more gross approximation to assume all adverse changes in transition temperature which takes place in low alloy steels are due to temper brittleness, without taking the appearance of the fracture ihto account. This has been a tendency with some American authors[30][19][63][64]. Jaffe and Buffum[63] have shown that heating a nickel-chrome

steel at 675°C after 48 hours embrittling at 500°C first restores the transition temperature to that of the tough steel. Prolonged heating then increases the transition temperature until after 250 hours it is raised to that of the embrittled steel. They attribute this effect to 'reversion', a phenomenon common in age hardening systems, but do not give any evidence to show that they are in fact dealing with temper brittleness. This is considered further in chapter VI below. It is possible to visualise other reactions in the steel which lead to either an increase in transition temperature, or to an intergranular fracture, but these can be distinguished from temper brittleness. Overheating, which gives intergranular fractures, is a permanent effect which cannot be removed without heating the steel into the austenitic range. Ferrite grain growth, which raises the transition temperature, is not reversible. Graphitization, which probably raises the transition temperature, and certainly lowers the room temperature impact value, can also be excluded, both because of the non-reversibility, and the fracture.

On the basis of this discussion, it will be assumed that temper brittleness is essentially a phenomenon taking place at the prior austenitic grain boundaries, leading to an intergranular fracture (under suitable

conditions). Where the intergranular fracture is not present it will be assumed that temper brittleness is absent. This does not exclude the possibility of the precipitate causing temper brittleness being located at points within the grains, but merely implies that the major effect is at the grain boundaries.

It is now possible to consider the descriptions of the low temperature fractures given in Tables IV, V and X.

In Table IV (page 59), it is seen that all the 'tough' steels gave cleavage fractures, and all the 'brittle' steels gave intergranular fractures. In Table V (page 61), the fractures of the brittle steels are seen to depend on the arsenic content of the steel. For XB, where the embrittlement caused a 20°C rise in transition temperature, the fracture contained about equal amounts of cleavage and intergranular facets; for WB, the 10°C change in transition temperature was accompanied by a substantial amount of intergranular fracture (about 25%). It is seen that the fracture is quite sensitive to slight changes in transition temperature, and also that these changes can be attributed to temper brittleness.

In Table X (page 72), it is seen that the fracture of the steel containing antimony, B, in the tough condition, was mostly intergranular. It is evident that this must

be caused by the embrittlement taking place at 620°C (see ref. 22, and also below), and that the high transition temperature of this steel is not solely due to the effect of the antimony in solid solution. In the experiments performed to test the reversibility of the phenomenon occurring in the antimony steel, by heating embrittled specimens at 620°C, it was found that even after 80 minutes at temperature the intergranular fracture persisted although the transition temperature must have been lowered by more than 250°C. This confirms the earlier suggestion.

The fractures of the other steels in this series showed no new features.

In the examination of various fractures of the EN 23 steels, it was noticed that the amount of intergranular fracture in a 'tough' steel depended on the precise heat treatment given the steel, and also on the grain size of the specimen. In order to investigate this further, a series of specimens of steel T (EN 23, 0.08% As) were oil quenched from 1250°C, and then tempered at various temperatures between 600 and 700°C, followed by water quenching. These were then notched and broken at -180°C, and the fractures examined.

It was found that as the tempering temperature was increased, the amount of intergranular failure in the

fracture decreased. By counting the grains in the field of view of the microscope at x 200, and taking 60 random fields per specimen it was possible to get a rough estimate of the percentage intergranular failure. The points derived from these estimates were found to lie on smooth curves, as shown in Fig. 23. Two series of specimens were used, with 1 and 24 hours tempering time. The immediate observations in relation to these curves are:- (1) the amount of intergranular fracture increases with decreasing tempering temperature, and decreases with increasing tempering time; (2) at 620°C the percentage of intergranular fracture is very considerable at both times, and is much more than that found in the fine grained steels used in the impact tests (in this case it was estimated to be less than 5%).

There are two possible reasons for the effects occurring. Either the steel is embrittled on heating through the range 400-600°C, and subsequent annealing reduces the embrittlement, resulting in the decreasing amounts of intergranular fracture, or (2) the steel embrittles at the tempering temperature, and subsequently 'overages'(see refs. 17 and 19). In either case, the embrittlement takes place to a much greater extent in coarse grained steels than in fine grained steels. The specimens used here had a grain size of 0-2 (ASTM) as

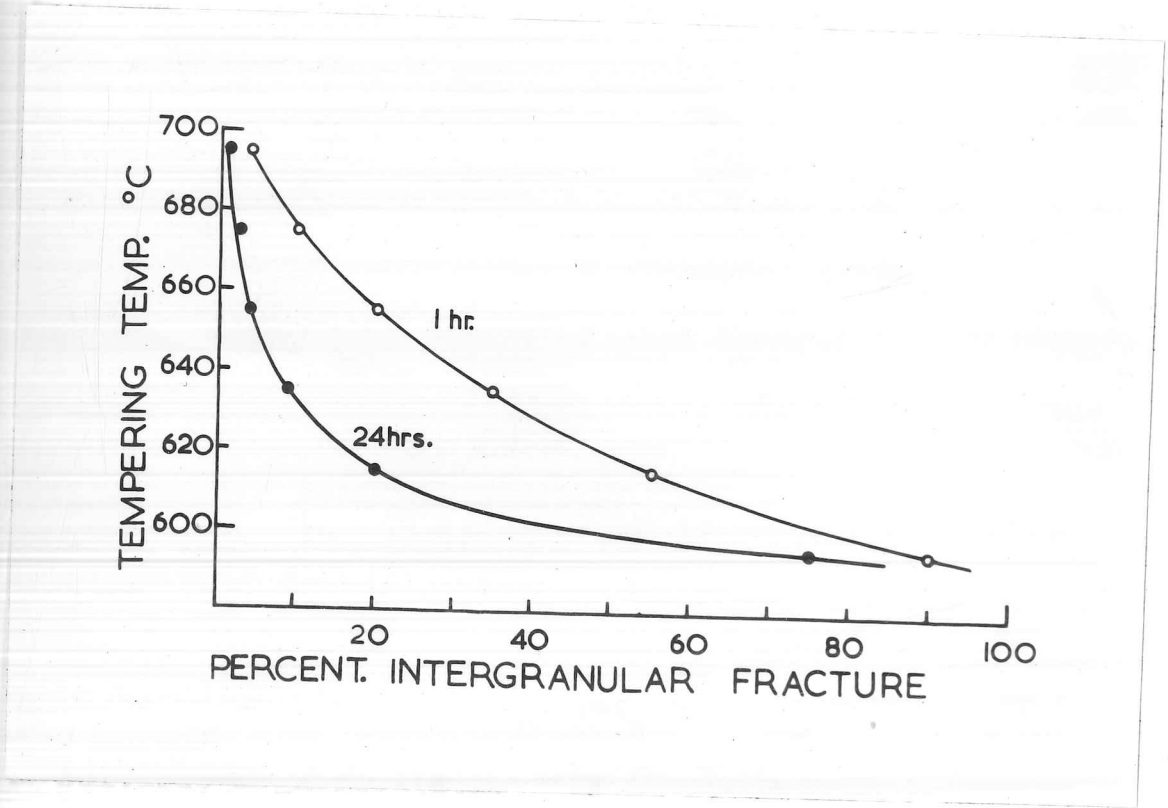

TEMPERING TEMP. °C
700
680
660
640
620
600
1 hr.
24hrs.
20
40
60
80
100
PERCENT. INTERGRANULAR FRACTURE

Fig. 23

compared with 8 in the impact tests.

The first alternative is thought to be unlikely, as the specimens were tempered in a salt bath, where the time of heating through the critical range was only about two minutes. Further, specimens heated in a tube furnace (heating time about 10 mins.) showed similar effects, with only slightly greater amounts of intergranular fracture. It seems likely therefore, that the second alternative is the correct one, namely, that the steel embrittles and subsequently overages at temperatures up to the $Ae_1$ point. However, the changes in transition temperature cannot be very large, as was demonstrated above.

It was not possible to estimate the relative amounts of intergranular and cleavage fracture in the fine grained steels used in the impact tests with any accuracy, because of the difficulty of examining the steel at a suitable magnification. It is clear from Tables IV, V and X, that the effects are not at all marked when the grain size is so fine. It is also noticeable that the steel T used in the experiments on cleavage fracture described in the first part of this chapter, does not fall on either of the curves given in Fig. 23. In this case the specimen contained only 5% intergranular fracture after 1 hour at 640°C. It is considered that the smaller

grain size 0-3 but mostly 3 A.S.T.M. accounts for this discrepancy.

Temper Brittleness in Plain Carbon Steels.

Another feature of temper brittleness which was elucidated by fracture examination was that of the temper brittleness of plain carbon steels. Jaffe and Buffum(30) suggested that the high transition temperatures of plain carbon steels were due to the fact that they were temper embrittled, even when quenched from the tempering temperature. They showed also, that when a plain carbon steel, hardened and tempered at 640°C, was given a severe embrittling treatment (48 hours at 480°C), the transition temperature was only slightly raised. They interpreted this as meaning that the embrittlement of the steel, even after quenching from 640°C was so great that the further treatment at 480°C had little effect. It is obvious that unless the brittle fractures of these steels were intergranular they could not be considered to be temper brittle in the same sense as alloy steels.

The following experiment was conducted to investigate this hypothesis:- specimens of a plain carbon steel (B.S. EN 8) with 0.4% carbon, and 0.65% manganese were used, These were quenched in brine from 1000°C, tempered 1 hour at 630°C and water quenched. Some were

then 'embrittled' by heating at 480°C for 24 hours. After breaking notched samples at -180°C the fractures were examined. In both sets of specimens the fractures were predominantly cleavage, but the specimens treated at 480°C did contain a slight amount of intergranular fracture. A typical area from each set of specimens is shown in Fig. 22. ((a) refers to the 'tough' steel, and (b) to the 'brittle' steel). The hypothesis of Jaffe and Buffum, appears to be erroneous, and it can be concluded the high transition temperatures of plain carbon steels are not a result of temper brittleness. The slight increase in the percentage intergranular fracture due to the 'embrittling' treatment may indicate that the small amount of manganese in the steel confers a very slightly susceptibility.

Conclusions.

(1) As far as is known, a prior austenite grain boundary in tempered martensite is characterised by (i) large carbide particles and (ii) a change in ferrite orientation, with no simple crystallographic relationship. There are other possibilities, e.g. segregation of alloying elements inherited from the austenising treatment (which occurs in burning and overheating) and inclusions will tend to be located in the grain boundaries. When

the steel is embrittled there will also be some form of precipitate located there. These features are all normal grain boundary features.

(2) The experimental evidence shows that a 'tough' steel when fractured at -180°C has a special type of cleavage fracture. This is shown to be associated with the structure of the ferrite (which is derived from the martensite). The ferrite grains (about 1$\mu$ diameter) are associated in groups about 60$\mu$ diameter (for this particular grain size) in which they all have approximately the same orientation. There is some microscopic evidence that the boundaries of these regions are characterised by carbide particles larger than the average, and are thus similar to the austenite grain boundaries. It seems reasonable to suppose that the effective ferrite grain size is 50$\mu$ rather than 1$\mu$ i.e. A.S.T.M. grain size 6 rather than 14 . As the austenitic grain size decreases, so the size of the uniformly orientated regions decreases. It is suggested that the variations in size of these ferrite ares, together with the change in particle size distribution of the carbides, controls the effect of the austenitic grain size on the properties of quenched and tempered steels.

(3) The presence of intergranular facets in the brittle fracture is shown to be a sensitive criterion for

temper brittleness. The change from cleavage type fracture to intergranular fracture is shown to be continuous but rapid.

(4) The number of intergranular facets in the fracture of EN 23 steels, tempered in the range 600-700°C is shown to decrease as the tempering temperature increases, and this is interpreted as demonstrating that temper embrittlement takes place to a slight extent in this range of temperature. The amount of embrittlement decreases as the austenite grain size decreases, and also as the tempering time increases.

(5) Plain carbon steels, when quenched and tempered, and then fractured in a brittle manner, show cleavage and not intergranular failure, independently of the 'embrittling' treatment. They are not therefore susceptible to temper brittleness in the same sense as alloy steels.

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Parts of this chapter have been published. A.R.Entwisle, J. Iron and Steel Inst., Vol. 169, pp. 36-38. (see Appendix C).

# CHAPTER VI

## THE EFFECT OF METALLURGICAL STRUCTURE ON THE SUSCEPTIBILITY TO BRITTLENESS.

This chapter is concerned with the effect of austenite grain size and hardness (as obtained by various tempering times at 620°C) on the displacement of transition temperature. These are two of the principal metallurgical variables which are likely to have any important effect.

### Austenite Grain Size.

The effect of austenite grain size on temper brittleness as measured in room temperature impact tests is well known[2][3][4], but whether this represents a real or only an apparent increase in susceptibility has not been made clear. Some data given by Herres and Lorig[65] and by Jaffe[66] suggest that the displacement due to a given embrittling treatment is increased.

In order to clarify the position, and also to assist in the correlation of the impact tests with the low temperature tensile tests, the transition curves were determined for two very coarse grained steels.

Bars of steels S and V (EN 23 with 0.021% and 0.255% As respectively) were austenised at 1150°C for 90 minutes, and then oil quenched. This produced an

austenitic grain size of 1-3 (A.S.T.M. scale). These bars were then tempered two hours at 620°C, followed by oil quenching, and some were then embrittled at 525°C for 4 hours or 250 hours. The transition curves were determined. These are given in Fig. A9, and the transition temperatures etc. are recorded in Table XIII. Also set out in the table are the equivalent results for the fine grained steels (from Table IV). From the transition temperatures it is obvious that the susceptibility is much increased by the increase in austenitic grain size; the displacement for both steels is increased by a factor of two.

The coarse grained steel S is about as susceptible as the fine grained steel V. The fractures show that both the steels in the 'tough' state were somewhat embrittled, more so for the steel containing the higher arsenic. This is to be expected from what has been shown in Chapter V. The high transition temperature of steel V ('tough') must be partly due to this embrittlement.

The maximum impact values are less for the coarse than the fine grained steels, and the slopes of the transition curves are also much less. The change in maximum impact value is reflected in the room temperature tensile properties (see Chapter VII). Here again is evidence of the effect of embrittlement on room temperature

Table XIII

| Designation (EN23) | Vickers Hardness | | Grain Size | Transition Temperature(°C) | M.I.V. | Fracture |
|---|---|---|---|---|---|---|
| | O.Q. | As Tested | | | | |
| S | 608 | 289 | 1-3 | -86 | 59 | Cleavage and Intergranular |
| SB | " | 286 | " | +34 | 58 | Intergranular |
| SB250 | " | 278 | " | +46 | 58 | Intergranular |
| S | 609 | 284 | 8-9 | -112 | 65 | Cleavage |
| SB | " | 281 | " | -42 | 65 | Intergranular |
| V | 604 | 298 | 1-3 | +30 | 56 | Mostly Intergranular |
| VB | " | 299 | " | +206 | 43 | Intergranular |
| VB250 | " | 289 | " | +230 | 33 | Intergranular |
| V | 596 | 291 | 7-8 | -78 | 66 | Mostly Cleavage |
| VB | " | 289 | " | +46 | 64 | Intergranular |

Steel S contains 0.021% As; Steel V contains 0.255% As.

properties other than in notched bar tests.

It is immediately evident that coarse grained steels have less grain boundary area than fine grained steels. Hence for a given volume of precipitation occurring at these boundaries, there will be a greater thickness of material at a grain boundary of a coarse grained steel. It is profitable to carry out some simple calculations on the quantities of material involved in grain boundary reactions.

Let it be assumed that the embrittling constituent is $Fe_3P$; for 1.c.c. of an alloy of iron and phosphorus containing 0.020% P:-

$$\text{Volume of } Fe_3P = \frac{W}{w} \times \frac{D_o}{D_1} \times 2 \times 10^{-4} \text{ c.cs./c.c. metal}$$

$$\text{Thickness of grain boundary film } T = \frac{W}{w} \times \frac{D_o}{D_1} \times \frac{2 \times 10^{-4}}{A} \text{ cms.}$$

Where W is the molecular weight of $Fe_3P$ (198.8)

" w " " " " " P (55.8)

$D_o$ is the density of $Fe_3P$ (6.74 gms./cu.cm.)

$D_1$ " " " " Fe (7.87 gms./cu.cm.)

A is the grain boundary area (sq.cms./cu.cm.)

(Values taken from "Metals Handbook" 1948, and "International Critical Tables").

This is of course assuming that all the phosphorus forms $Fe_3P$, and that all the $Fe_3P$ is present as precipitate at

the grain boundaries. The values of A for different A.S.T.M. grain sizes are given below, together with the calculated values for t.

It is difficult to estimate what thickness of film is required to produce the effects on the impact properties, but as the C axis of the unit cell of $Fe_3P$ is (9Å, it will be assumed that 50Å are required, i.e. 5 unit cells. This value of 50Å is sufficiently small to be impossible to observe with an optical microscope as a separate phase, but is considered large enough to give rise to the observed etching effects.

Table XIV.

| A.S.T.M. Grain Size. | A Sq.Cms./cu.cm. | t(Å) |
|---|---|---|
| 1 | 9.5 | 1,600 |
| 4 | 26.7 | 560 |
| 8 | 107 | 140 |
| 9 | 151 | 100 |

The work of Herres and Elsea is interesting in this respect, since they found that by reducing the phosphorus content of a 1.5% Mn steel, or of a 1% Mn, 0.75% Cr

steel, from 0.02% to 0.005% P, the displacement of the transition temperature was very much reduced. This is equivalent to reducing the film thickness from 140 to 35 Å. This may mean that phosphorus is present, in some form, at the grain boundaries of a temper brittle steel.

There is an alternative to this theory. The mechanical effects may be due to increasing the area of grain boundary covered by the precipitate, rather than to increasing thickness. If this is the case, the calculations lead to the same conclusions as to the effect of grain size, and composition.

It is also interesting to note that $Mn_3P$, $Cr_3P$, and $Ni_3P$ are all isomorphous with $Fe_3P$, and the figures given in the table apply approximately to these compounds.

The analysis given above is equally valid for any added element, but the values for t must be multiplied by a constant factor, depending on the element, and the compound assumed to be formed. In the case of the results given in Table XIII it is seen that changing the grain size from A.S.T.M. 8 to 1, increases the film thickness by a factor of ten, and for steel SB(EN 23, 0.021% As), increases the displacement of the transition temperature from 70 to 120°C. Increasing the arsenic from 0.021 to 0.255% (a factor of about ten in grain

boundary film thickness assuming all the arsenic is present at the boundary), increases the displacement from 70 to 124°C. This may be coincidental, but it must be borne in mind when considering the ultimate cause of temper brittleness. The same argument is valid in the case where only a given fraction of arsenic is assumed to precipitate at the grain boundary. It is only intended here to draw attention to the actual quantities involved in grain boundary reactions, and to show the effect of grain size.

Effect of Tempering Time.

In general, the softer the product of tempering, in alloy steels, the lower is the susceptibility to temper brittleness as measured in room temperature tests. Jaffe and Buffum(64) have shown, that for different hardnesses obtained by using different tempering temperatures, the displacement of transition temperature due to a given embrittling treatment is nearly independent of hardness. In view of the importance of this conclusion, it was considered advisable to conduct a similar series of experiments, in which the different hardnesses were obtained by using different tempering times at the same tempering temperature. In this way it was hoped to avoid effects due to embrittlement taking place at the lower tempering temperatures.

A series of specimens of steels T and V (EN 23, 0.085% and 0.255% As respectively) were oil quenched after one hour at 900°C. These were then tempered at 620°C for ½, 8, 32, or 128 hours, and water quenched. Half of each lot was then embrittled for 4 hours at 525°C, followed by water quenching. The transition curves were determined for the whole series. These are recorded in Figs. A10-A13. The actual transition temperatures, hardness and maximum impact values are given in Table XV.

The features of these results are:- (1) the 'tough' transition temperature is virtually unaffected by increasing the tempering time at 620°C above 2 hours; (2) the displacement of the transition curves due to the embrittling treatment steadily decreases as the tempering time at 620°C is increased. The slopes of the transition curves, and the maximum impact values, both increase as the tempering time increases. The first two effects are clearly shown in Figs. 24 and 25. Ta, is the 'tough' transition temperature, and Tb, the 'brittle' transition temperature. $\Delta T$, the displacement, is the numerical difference between Ta and Tb. The displacement ($\Delta T$) decreases linearly with log (tempering time). The greater susceptibility of steel containing 0.255% As also becomes less apparent as the tempering time increases.

Table XV

| Designation | Time at 620°C (hours) | Vickers Hardness O.Q. | As Tested | Embrittled | $T_a$ (°C) | $T_b$ | M.I.V. (Mean) | Fracture 'Tough' | Fracture 'Brittle' |
|---|---|---|---|---|---|---|---|---|---|
| Steel T EN 23+ 0.085% As. | ½ | 611 | 309 | 310 | -82 | +4 | 60 | Cleavage and Intergranular | Intergranular |
| | 2 | 610 | 282 | 280 | -98 | -28 | 65 | Cleavage | Intergranular |
| | 8 | 614 | 279 | 277 | -94 | -30 | 68 | Mostly Cleavage | Intergranular |
| | 32 | 616 | 258 | 257 | -94 | -44 | 71 | Cleavage | Intergranular |
| | 128 | 602 | 235 | 234 | -92 | -54 | 77 | Cleavage | Mostly Intergranular |
| Steel V EN 23 + 0.255% As. | ½ | 603 | 306 | 305 | -58 | +68 | 61 | Cleavage and Intergranular | Intergranular |
| | 2 | 596 | 291 | 289 | -78 | +46 | 65 | Mostly Cleavage | Intergranular |
| | 8 | 612 | 282 | 279 | -70 | +24 | 70 | Mostly Cleavage | Intergranular |
| | 32 | 610 | 257 | 253 | -76 | -2 | 77 | Cleavage | Intergranular |
| | 128 | 602 | 240 | 239 | -74 | -22 | 78 | Cleavage | Mostly Intergranular |

A.S.T.M. grain size was 8 or 7-8 for all steels.

Data for 2 hours at 620°C taken from Table IV.

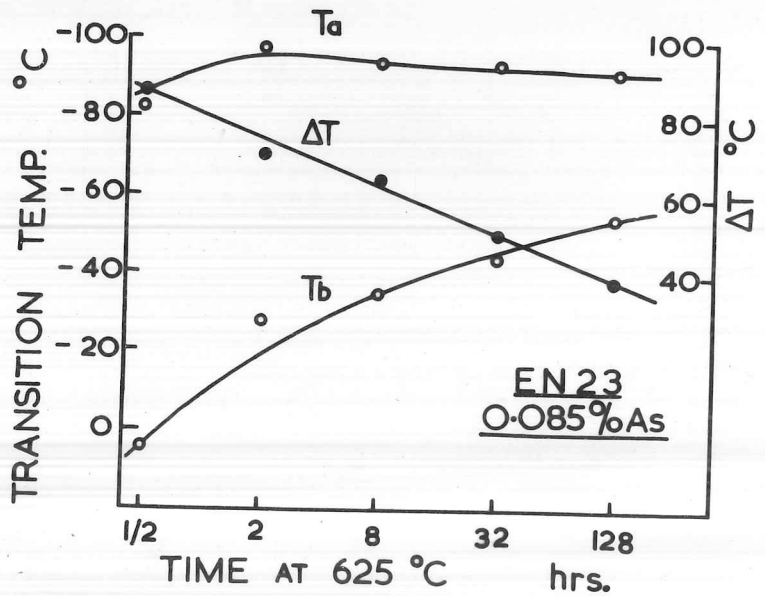
TRANSITION TEMP. °C
-100
-80
-60
-40
-20
0
Ta
ΔT
Tb
100
80
60
40
ΔT °C
EN 23
0·085% As
1/2
2
8
32
128
TIME AT 625 °C hrs.

Fig. 24

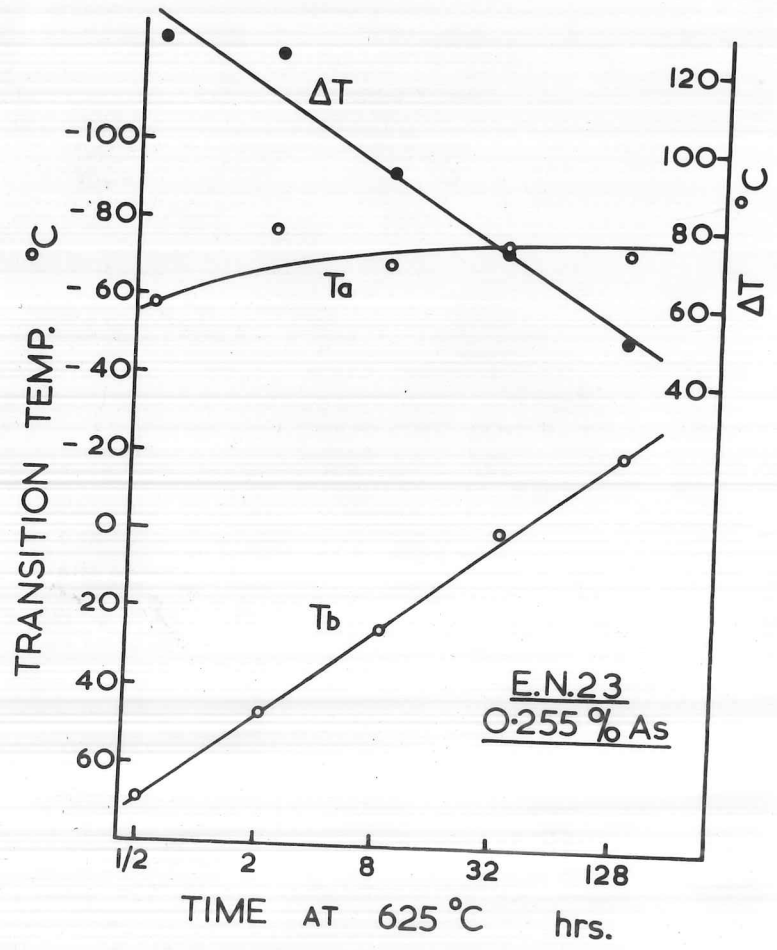
ΔT
Ta
Tb
-100
-80
-60
-40
-20
0
20
40
60
120
100
80
60
40
°C
ΔT
TRANSITION TEMP. °C
E.N.23
0·255 % As
1/2
2
8
32
128
TIME AT 625 °C hrs.

Fig. 25

When the $\Delta T$ curves are extrapolated to $\Delta T = 0$, i.e. when the steels have no susceptibility to temper brittleness, the times are found to be nearly the same; 950 hours for 0.088% As, and 800 hours for 0.255% As. The difference between them is little greater than the probable error of the extrapolation.

Considering the 'tough' steels, it is seen that after ½ hour at temperature, the brittle fractures had roughly equal amounts of cleavage and intergranular fracture, and that as the tempering time increased, the amount of intergranular fracture decreased. At 32 and 128 hours virtually no intergranular fracture was present. For this series of steels, the time of heating to the tempering temperature was rather long, (about 20 minutes), and it is thought that the rather large amounts of intergranular fracture in the ½ hour steels was mostly due to this. When considering the effect of tempering time on the 'tough' transition temperatures, this must be borne in mind. It may account for the bend in the curves ($T_A$) at the shorter tempering times.

The normal microstructures of the 'tough' steels showed only slight changes as the tempering time was increased. When replicas of the surface were examined on an electron microscope, these changes were found to be much more clearly defined. Figs. 26 and 27 show typical

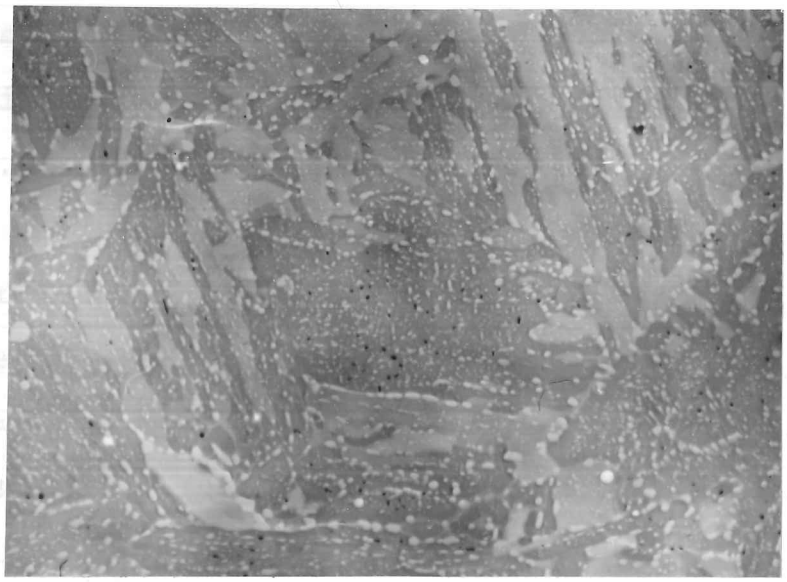

Fig. 26 x 5000

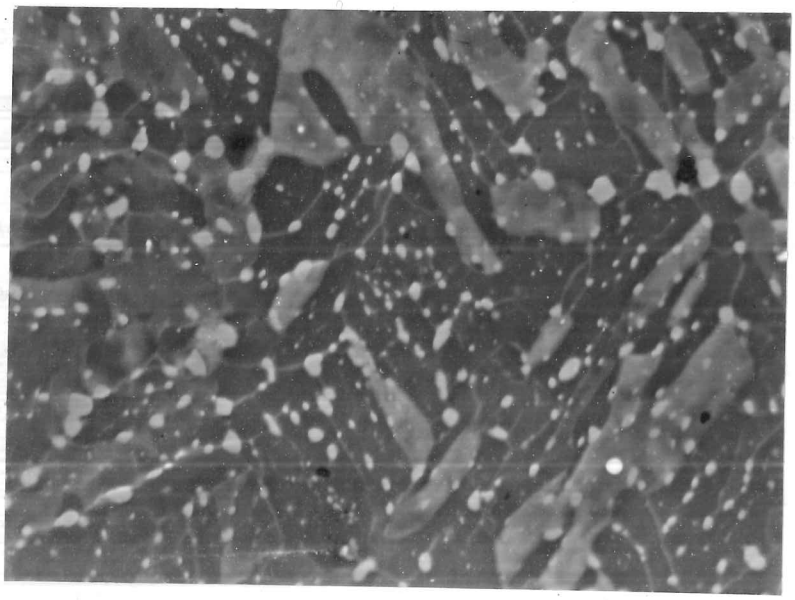

Fig. 27 x 5000

areas of the steel T after 2 and 128 hours at 625°C respectively. The specimens were polished, and etched in Nital; formvar replicas were then taken of the surface. The contrast derived from the replica is such that those parts of the metal left protruding above the general surface level, (i.e. not rapidly attacked by the etchant), are light in tone, and the normal surface is dark. In both figures the carbide particles show up as light spots. In Fig. 26, the light areas are ferrite not as rapidly attacked as the rest of the matrix. As the rate of attack by the etchant depends on the crystallographic orientation of the ferrite, it may be inferred that these light ares are areas of uniform ferrite orientation, i.e. they correspond to the ferrite areas discussed in Chapter V. After 128 hours at 620°C the orderly array of these areas is broken down, but the effect can still be seen on individual ferrite grains.

The carbide particle size is much increased by the increased tempering, and the ferrite grain diameter (obtained from other photographs at higher magnifications), is increased from about 0.8$\mu$ to 1.5$\mu$. The increase in ferrite grain size leads to a general breaking down of the ferrite areas, since imperfections in the orientation will be accentuated. Free growth of the grains, is however, restricted by the carbide particles. These

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combined effects of ferrite grain growth and carbide part-growth apparently leave the transition temperature unaltered.

It is interesting to note that the ferrite grain boundaries are left raised above the general level of the surface. This may indicate that carbide films are present, which are unattacked by the etchant.

The traces of the austenite grain boundaries, which are clearly shown by the larger carbide particles in Fig. 26, are nearly removed by the long time tempering (Fig. 27). This may account for the change in susceptibility.

The 'brittle' steels, show one important feature in the fractures. At the longest tempering times the low temperature fractures definitely showed an increase in the amount of cleavage fracture present (5-10%). This does confirm the conclusion that a real reduction in susceptibility is obtained by the long time tempering treatment.

It was considered necessary to show that the reduction in susceptibility was independent of the embrittling time, i.e. to show that it was not due to a decrease in the rate of embrittlement. Two specimens, TJ, and VLB (see Table XV) were embrittled at 525°C for 180 hours, followed by water quenching. These were then fractured at -30°C, and -20°C respectively. It

was found that only a very slight increase in transition temperature about 10°C had taken place due to this long embrittling treatment, as compared with the 4 hour treatment. It is certain from this, that the reduction in susceptibility is not an effect of alteration in the rate of embrittlement.

It is now proposed to consider these results in relation to those of Jaffe and Buffum(64) and earlier workers, and then to proceed to possible explanations of the phenomena observed.

Both Houdremont and Schrader(7) and Jones(9) showed that the susceptibility ratio is reduced after either repeated tempering above 600°C, or prolonged holding above 600°C. This cannot be regarded as definite evidence that the susceptibility is reduced. Jaffe and Buffum(64) showed that the displacement of transition temperature is hardly affected by the hardness of the steel, if these hardnesses are obtained by using different tempering temperatures (in the range 500-675°C). Their results (displacements $\Delta T$ v hardness) are plotted in Fig. 28, together with those given in Table XIV. The steel they used was SAE 3140 (0.77% Cr, 1.26% Ni, 0.39% C.). It is evident that there is some tendency for the susceptibility to increase with decreasing hardness for this steel. This may be spurious, as this curve cannot be considered as

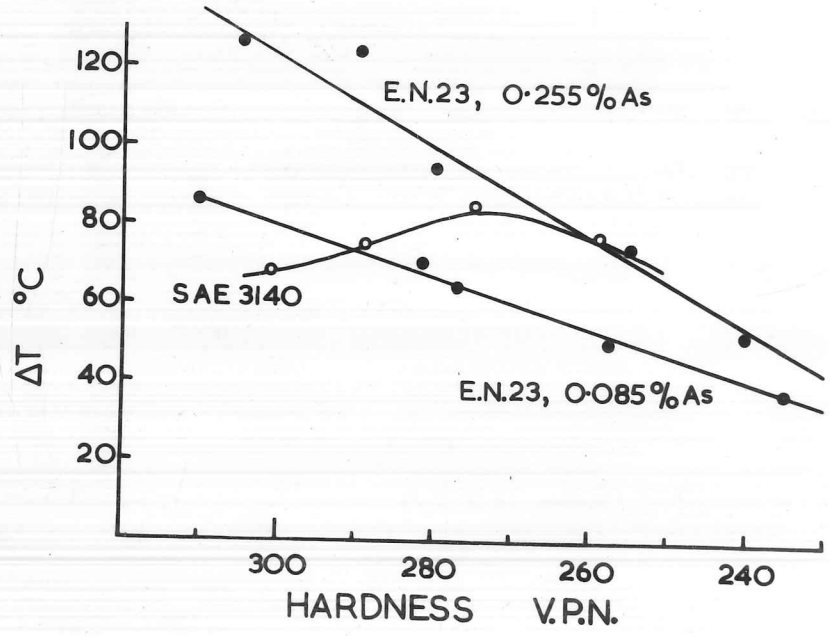

120
100
80
60
40
20
ΔT °C
E.N.23, 0·255% As
SAE 3140
E.N.23, 0·085% As
300
280
260
240
HARDNESS V.P.N.

Fig. 28

accurate, since the points were taken from a graph in the original paper, and the hardness values have been converted from Rockwell C to Vickers.

The fact that the susceptibility of the SAE 3140 is low, is possibly due to the low tempering temperature (600°C) used; some embrittlement will have taken place in the tough steel, resulting in a decrease in the displacement. This does not affect the major conclusion however, that the processes leading to the reduction of susceptibility are much more dependent on the time at the tempering temperature, than on the actual temperature; i.e. the activation energy for the process is low.

There appear to be two possible explanations for the reduction of susceptibility. It was pointed out above, that the austenite grain boundaries become less clearly marked as the tempering time is increased. It is possible that sites for nucleation of the precipitate are thereby lost, and this results in either a smaller amount of precipitation, or a more uniform distribution of the precipitate. In either case, a decrease in susceptibility would follow. The alternative to this theory is based on the concept of homogenisation. It can be assumed that precipitation occurs mainly at the austenite grain boundaries, because

a suitable concentration of element(s) is built up there whilst the steel is austenitic. When the steel is heated in the critical range (say 300-600°C), precipitation can take place most readily where these concentrations occur. Prior annealing above the critical range will lead to a more even distribution of the segregated elements (it is not necessary, at this stage to postulate where they are redistributed), and consequently to a smaller amount of precipitation at the austenite grain boundaries.

This latter hypothesis seems the more likely, since it also gives a reason for the predominance of the effect at the austenite grain boundaries.

Another phenomenon reported by Jaffe and Buffum(63) must also be considered in relation to the effect of these high temperature treatments. They have shown that if a steel (SAE 3140), is embrittled at 525°C, and subsequently heated to 675°C, the following changes take place:- the transition temperature is rapidly lowered to that of the 'tough' steel (in less than one hour); it then rises slowly, until after 250 hours, it reaches that of a severely embrittled steel. Further, if specimens of the 'tough' steel are heated for 250 hours at 675°C, the transition temperature is found to have risen to the same value. They attribute the first

phenomenon to reversion, a feature of some age hardening systems. They consider the second effect to be due to embrittlement at this high temperature.

The structural changes which take place at these high temperatures, tend to cast some doubt on this theory. Thus, the hardness is lowered from 241 to 180 V.P.N. Some change in transition temperature might be expected due to causes other than temper brittleness.

These ideas were confirmed by the examination of suitably heat treated steel. A sample each of steel A and AB (see Table X), were heated at 675°C, for 64 hours, and then quenched, (V.P.N. 220). These were then notched and fractured at -180°C. An examination of the fractures of both steels showed that both were cleavage, with no intergranular facets present in either; i.e. the 'brittle' steel had become 'tough' and the 'tough' steel remained 'tough'. There is no evidence therefore, to substantiate the conclusions of Jaffe and Buffum, that reversion of temper brittleness occurs at tempering temperatures approaching $Ac_1$, leading to increases in the transition temperature.

Conclusions.

(1) A change in austenite grain size from A.S.T.M. 8 to 1, very greatly increases the susceptibility of the steels studied to temper brittleness. This effect can

be attributed to the change in grain boundary area. On the assumption that a layer of precipitate 50Å thick can cause the measured effects on the mechanical properties, it is shown that elements present in amounts less than 0.01% could be the ultimate cause of temper brittleness.

(2) Annealing the steels studied at 620°C for periods up to 128 hours, causes a substantial decrease in the susceptibility, without altering the transition temperature of the 'tough' steel. This can be explained on the assumption that segregation whilst the steel is austenitic, causes temper brittleness during the subsequent heat treatment. The 620°C treatment is thought to disperse these local concentrations.

(3) The theory that the deterioration of the impact properties of steel annealed at 675°C is due to reversion, is shown to be untenable.

# CHAPTER VII

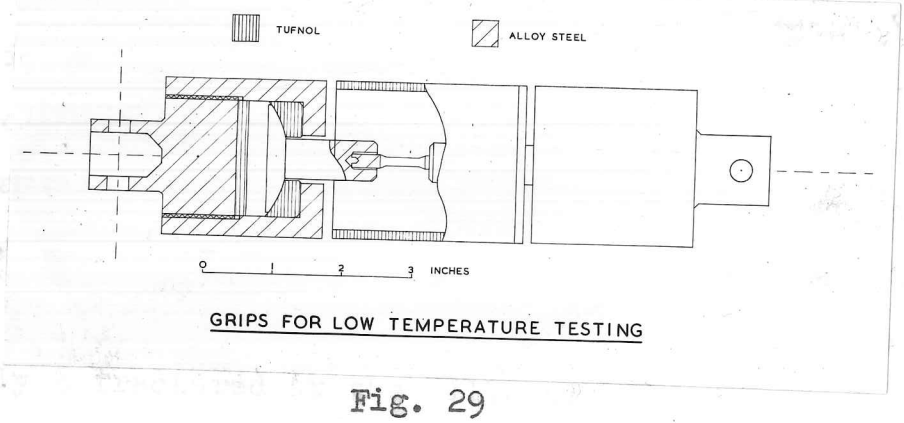
## LOW TEMPERATURE TENSILE TESTING.

From the analysis given in Chapter II, it has been shown that the tensile properties of alloy steels at low temperatures should show marked changes when severely temper embrittled. Five series of tests were carried out to investigate this prediction.

### Apparatus.

There are two requirements for the grips for the tensile testing of materials at low temperatures: (1) thermal insulation of the specimen from the testing machine, and (2) an arrangement to ensure that the specimen is stressed axially. The grips shown in Fig.29 were designed with these purposes in mind. The metal portions were made of heat treated steel of the Vibrac type, and the thermally insulating parts were made of Tufnol. The separate parts of the assembly are shown in Fig. 30.

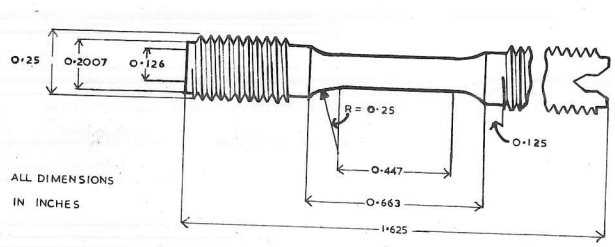
The specimens used were 1/80th square inch in cross-sectional area, as shown in Fig. 31, and with threaded ends ¼ inch diameter (B.S.F.). These were prepared on a universal grinding machine, and the gauge length and the fillets were polished on emery paper down to 4 O's. During this polishing the gauge length was




GRIPS FOR LOW TEMPERATURE TESTING

Fig. 29

Fig. 30




TENSILE SPECIMEN FOR LOW TEMPERATURES

Fig. 31

slightly tapered to the centre, so that the minimum cross-section at the centre, was about 0.0003" less in diameter than at the ends. This ensured that the specimen always broke near the middle of the gauge length. In the actual tests, 55 specimens were broken, and of these only 3 fractured at the fillets.

The testing machine used was a Tensometer type C, of two tons capacity, fitted with the axis vertical. Tests were carried out at a constant strain rate (4 in./in/hour, on the gauge length), the power being supplied by a small electric motor.

The sequence of operations adopted in testing was as follows:- the specimen (diameter measured to 0.0002") was screwed into the grips, and a small load was applied to it (about 0.2 tons). Liquid oxygen was then poured into the cup, and the level was maintained for 15 minutes. The liquid, after this time was boiling quietly, indicating that appreciable conduction was taking place between the oxygen, the specimen and its surroundings. The oxygen was then removed, and replaced with liquid nitrogen. The level in the cup was maintained for 10 minutes, and the test was then performed. During the cooling period the load on the specimen increased to about 0.4 tons. The testing time varied between 1 and 5 minutes, depending on the ductility

of the specimen, and the level of the nitrogen was maintained during the test. After fracture, the reduced diameter of the specimen was measured, and the fracture stress etc. were calculated from the autographic record obtained during the test.

In order to measure the temperature of the specimen at the commencement of the test, a hole was bored down the centre of one of the grips, and a thermocouple inserted in it. Measurement of the temperature at the end of the specimen showed that in the liquid oxygen, the temperature fell to -176°C (i.e. 7°C above the boiling point) in ten minutes. After this the temperature fell only very slowly (about 0.1°C per minute). When the oxygen was replaced with nitrogen, the temperature fell to -188°C in about ten minutes and remained constant at this value. In a special test, in which the test piece was bored out up to the inner end of the thread, the corresponding temperatures at this point were found to be -179° and -194°C. This means that the maximum temperature gradient possible along the gauge length of the specimen was 2°C., and was probably only 1°C. This was considered to be sufficiently accurate for these tests. This measurement of temperature was only carried out in two tests, the routine described above being applied in all cases.

Results of Tests.

EN 23, 0.255% As, A.S.T.M. Grain Size 1-3. The coarse grained impact specimens, used in the experiments described in Chapter VI were used for this series of tests. The fractured pieces of 'tough' specimens were embrittled for different times at 525°C in a small tube furnace, followed by water quenching. These were then made into tensile test pieces, and tested with the apparatus described, using liquid nitrogen as the coolant, during the actual straining. The results of these tests are given in Table XVI, which includes values of Yield Stress (Y.S.), Ultimate Tensile Strength (U.T.S.; the points for this curve are omitted, to avoid confusion with the other curves), "True" Fracture Stress (T.F.S., i.e. load at fracture divided by area at fracture), % Reduction of Area (R.A.), Diamond Pyramid Hardness (D.P.H.; determined on ends of the specimens after fracture, using 10 Kgs. load), and a brief description of the fracture.

These results show that as the time at 525°C is increased, the true fracture stress and the % reduction of area decrease, and the appearance of the fracture changes from fibrous to intergranular. The results are shown graphically in Fig. 32. Here the changes are clearly shown; the fracture stress and the reduction of

EN 23, 0.255% As. A.S.T.M. Grain Size 1-3

| Time at 525°C (Minutes) | Testing Temp. °C | Yield Stress | U.T.S. | T.F.S. | %R.of A. | D.P.H. | Description of Fracture |
|---|---|---|---|---|---|---|---|
| 0 | +20 | 51.2 | 59.3 | 115.1 | 61 | 299 | Cup and Cone, with some radial cracks. |
| 0 | +20 | 50.5 | 60.5 | 117.0 | 62 | 297 | " |
| 0 | -196 | 77.5 | 85.6 | 119.3 | 35 | 296 | Flat transverse fracture, with fine system of cracks |
| 90 | -196 | 77.5 | 84.7 | 92.0 | 7.9 | 297 | Fractured at fillet |
| 90 | -196 | 77.2 | 86.9 | 116.7 | 29 | 295 | Intergranular but dull in appearance |
| 240 | -196 | 77.5 | 86.4 | 97.8 | 11.7 | 296 | Intergranular |
| 240 | -196 | 77.0 | 85.2 | 95.5 | 10.8 | 299 | " |
| 960 | -196 | 75.4 | 79.4 | 84.0 | 5.4 | 294 | " |
| 960 | -196 | 75.2 | 80.8 | 84.1 | 4.0 | 299 | " |
| 3,840 | -196 | 72.2 | 73.2 | 75.9 | 4.0 | 289 | Intergranular, but large grain size |
| 3,840 | -196 | 77.6 | 81.6 | 86.4 | 5.5 | 292 | Intergranular |
| 7,200 | -196 | 76.6 | 82.3 | 89.2 | 7.8 | 287 | " |
| 7,200 | -196 | 76.6 | 81.5 | 85.5 | 4.7 | 287 | " |
| 14,400 | -196 | 77.4 | 76.6 | 77.8 | 1.5 | 286 | Intergranular, but large grain size |
| 14,400 | -196 | 77.2 | 79.4 | 86.8 | 6.4 | 288 | Intergranular |
| 14,400 | +20 | 51.7 | 59.8 | 92.2 | 43 | 285 | Dull Intergranular, with many grain boundary cracks |

All stresses in tons/sq.in. Hardness measured with 10 Kg.load

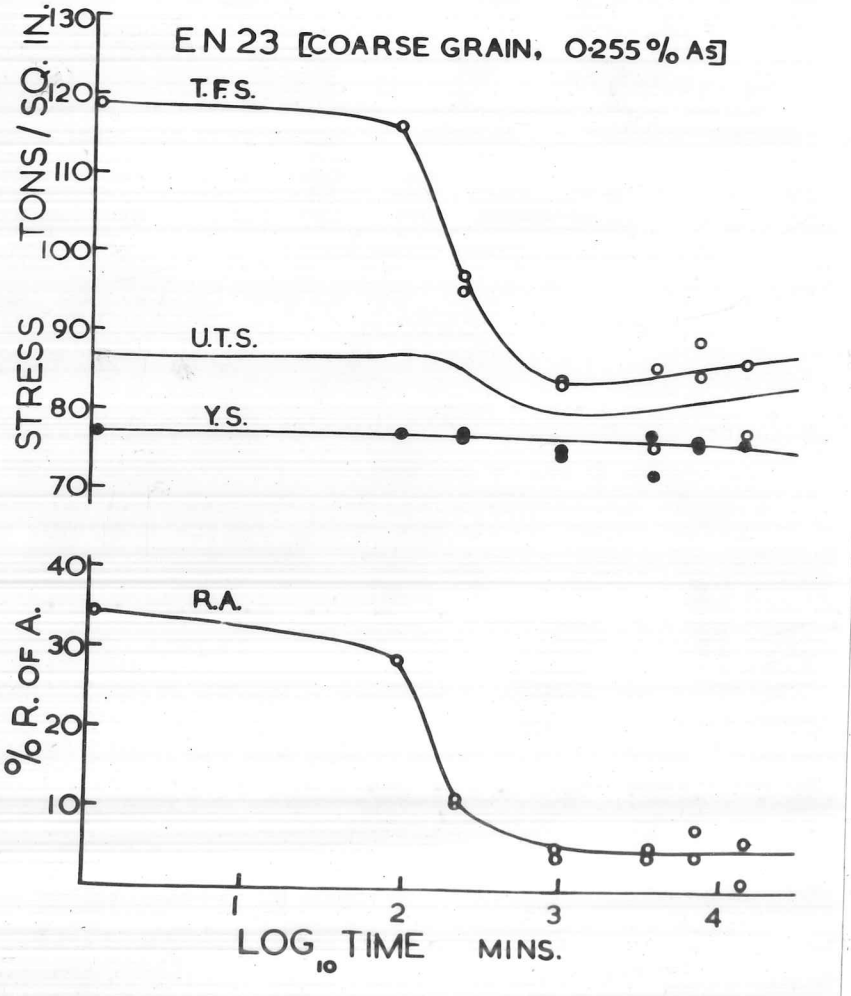

EN 23 [COARSE GRAIN, 0·255% As]
T.F.S.
U.T.S.
Y.S.
R.A.
STRESS TONS / SQ. IN.
% R. OF A.
LOG10 TIME MINS.
130
120
110
100
90
80
70
40
30
20
10
1
2
3
4

Fig. 32

area fall rapidly after 100 mins. embrittling time, and then fall gradually as the time further increases. The scatter in the values is probably due to variations in the austenitic grain size. The yield stress remains nearly constant, but the ultimate tensile strength falls somewhat after 100 mins. The drop in the U.T.S. takes place when specimens fracture before the load extension curve becomes horizontal.

Fig. 33 shows diagramatically the effect of increasing the embrittling time on the load extension curves of this steel. (The dotted line indicates the true load axis from which extensions should be measured, and is a characteristic of the testing machine.) The effect of progressive embrittlement on the load extension curves (at -196°C) is to arrest them prematurely, at successively lower extensions as the time at 525°C increases.

For the 'tough' steel the effect of changing the testing temperature from 20° to -196°C is also shown. The reduction in area is decreased by a factor of two, and the yield stress and the ultimate tensile strength are nearly doubled; the uniform elongation is slightly increased, and the yield point becomes very much more pronounced. The true stress at fracture is hardly altered. For the most brittle specimen, fracture occurred at a load less than the yield load, before the load had

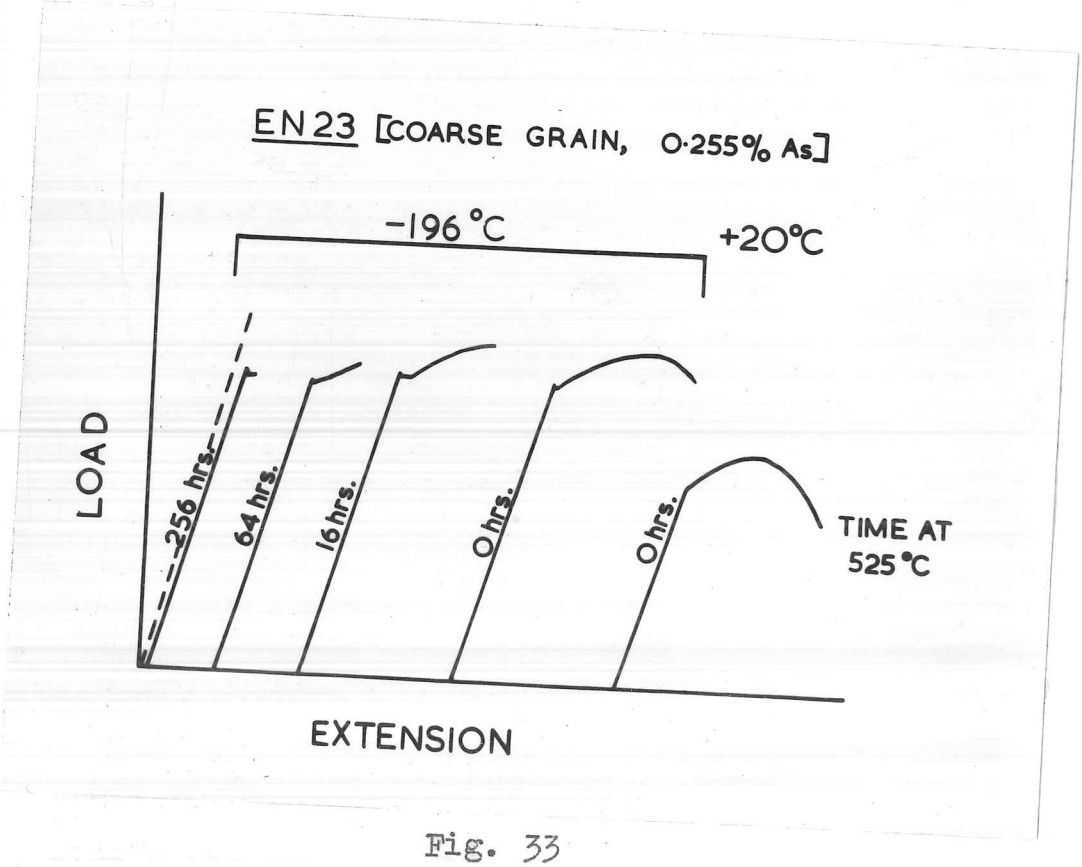

EN 23 [COARSE GRAIN, 0·255% As]
-196 °C
+20°C
LOAD
256 hrs.
64 hrs.
16 hrs.
0 hrs.
0 hrs.
TIME AT 525 °C
EXTENSION

Fig. 33

started rising again, following the onset of plasticity.

The specimens with low ductility were found to fracture at a stress in the range 80-90 tons/sq.in., and it is certain that these values must approach the true values of the intergranular brittle strengths for these materials. By pre-straining a specimen at room temperature, and subsequently fracturing it in liquid nitrogen, it was found possible to get a rough estimate of the effect of deformation on the intergranular brittle strength. This strength was found to be increased by 1.3 tons/sq.in. for each 1% of deformation. Thus for the specimen treated for 250 hours at 525°C, the brittle strength of the undeformed material was found to be 78 tons/sq.in. This corresponds to a notched bar transition temperature of 230°C (see Table XIII).

The fractures of the series of specimens showed interesting changes as the embrittlement proceeded. Fig. 34 showed the room temperature fracture of the non-embrittled steel, with the typical radial cracks, and the well developed shear fracture at the edge. At -196°C the same steel had a flat transverse fracture with no visible shear; many fine cracks were visible on the surface (Fig. 35). After 90 minutes at 525°C, the low temperature fracture was recognisable as inter-granular, but the surfaces of the grains were dull in

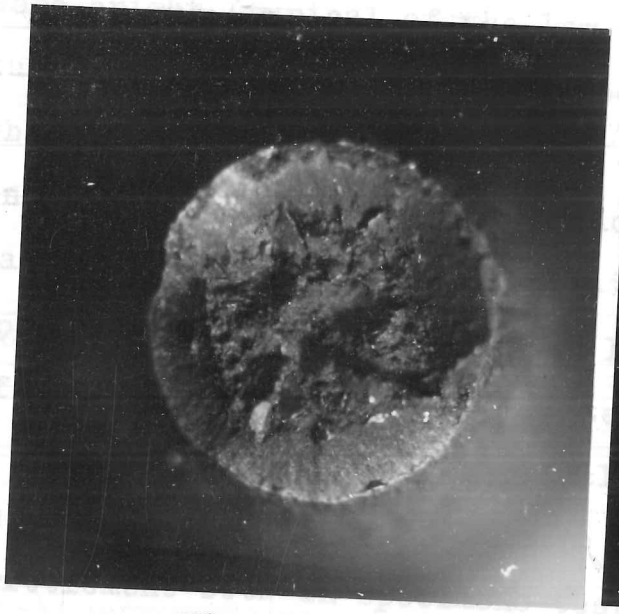


Fig. 34 x 25

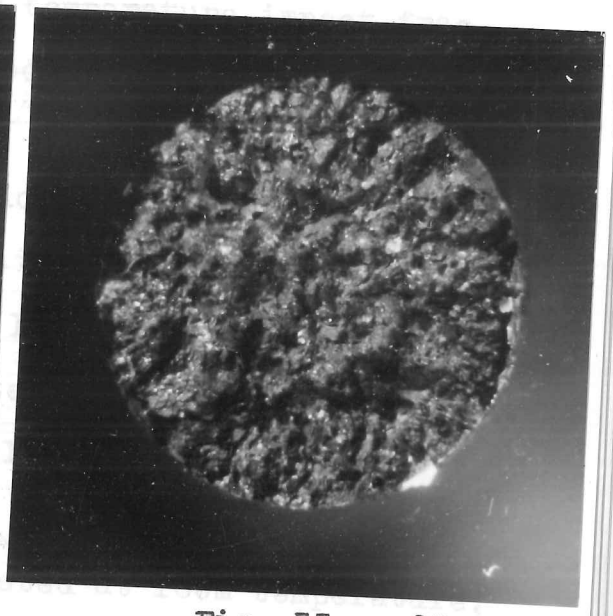


Fig. 35 x 25

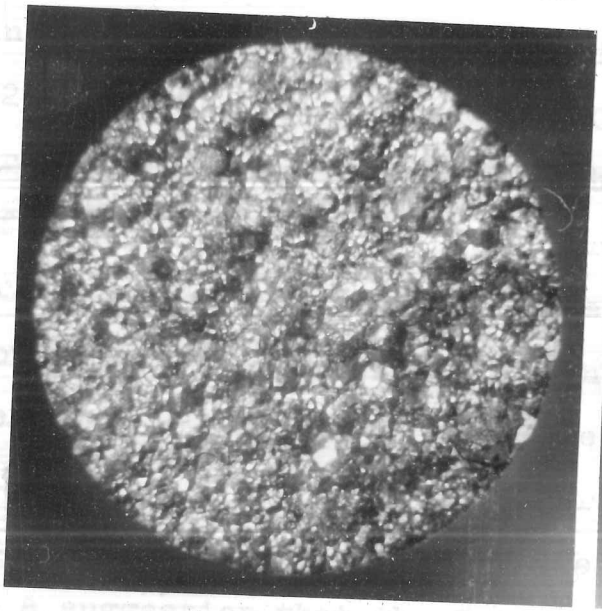


Fig. 36 x 25

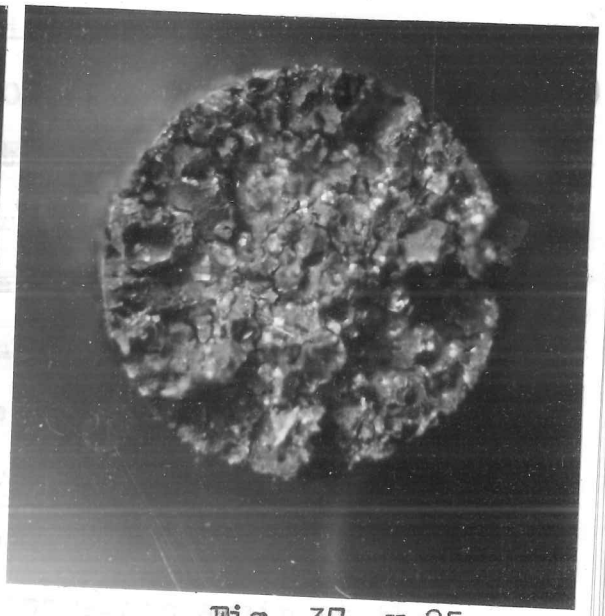


Fig. 37 x 25

appearance. After 120 hours the surfaces of the grains were bright (typical of the low temperature impact fractures), and the fracture appeared as shown in Fig. 36. The room temperature fracture of this steel is shown in Fig. 37. This was without doubt intergranular, with many deep cracks between the grains. The general appearance was dull, as for the low temperature fracture of the steel embrittled 90 minutes.

It can therefore be concluded that the fractures show changes which correspond to the progressive embrittlement both in specimens tested at room temperature, and at -196°C.

EN 23, 0.255% As, A.S.T.M. Grain Size 7-8. Specimens for treatment for this series were taken from the fractured impact specimens used in obtaining the data given in Table IV. The 'tough' specimens were embrittled at 525°C for various times up to 500 hours. The results are recorded in Table XVII. It is seen that the effects of the embrittlement are similar to those for the coarse grained steels, but in this case they are much less pronounced. The results are shown graphically in Fig. 38. Here again there is considerable scatter, but it is clear that both the fracture stress, the U.T.S., and the ductility fall with increasing embrittling time. There is a suggestion that the % R.A. increases again at the

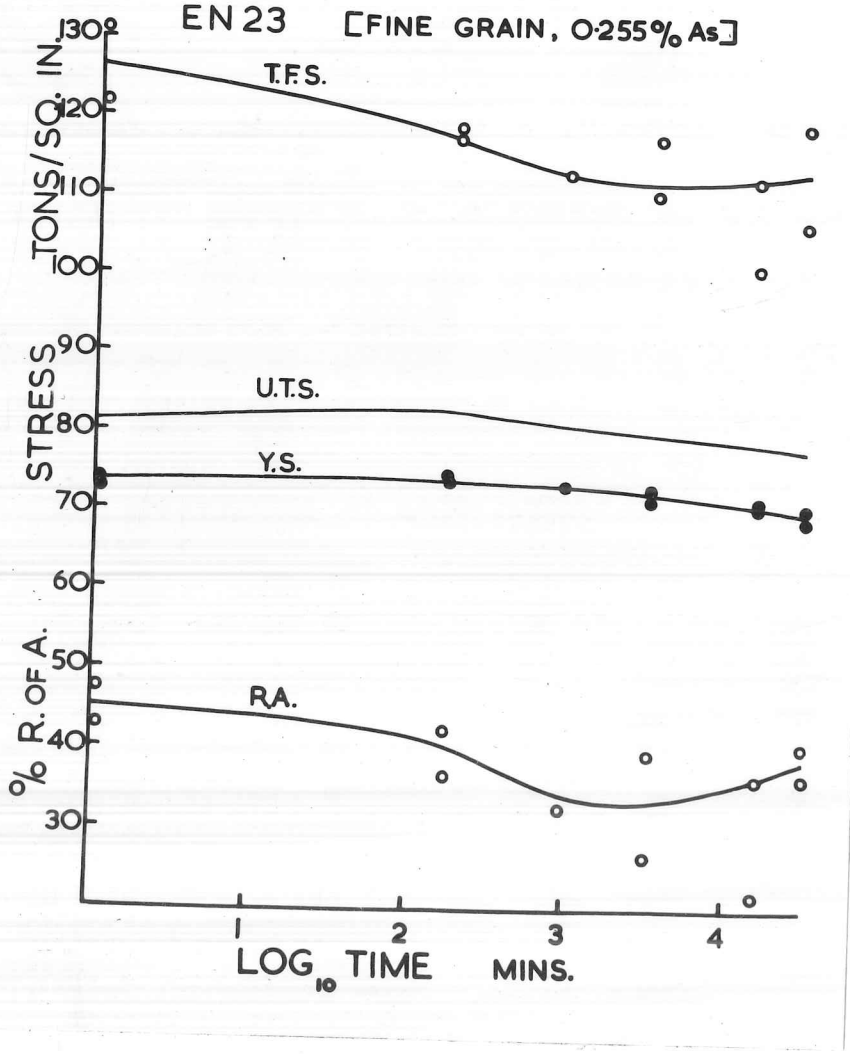

EN 23 [FINE GRAIN, 0·255% As]
T.F.S.
U.T.S.
Y.S.
R.A.
STRESS TONS/SQ. IN.
% R. OF A.
130
120
110
100
90
80
70
60
50
40
30
1
2
3
4
LOG10 TIME MINS.

Fig. 38

EN 23, 0.255% As, A.S.T.M. Grain Size 7-8

| Time at 525°C (Minutes) | Testing Temp. °C | Yield Stress | U.T.S. | T.F.S. | %R.of A. | D.P.H. | Description of Fracture |
|---|---|---|---|---|---|---|---|
| 0 | +20 | 46 | 54.4 | 115.0 | 66 | 287 | Cup and Cone; with radial fissures |
| 0 | -196 | 72.8 | 80.9 | 131.1 | 47.5 | 281 | Slight shear; fine system of cracks. Flat transverse |
| 0 | -196 | 73.6 | 80.8 | 123.7 | 42.7 | 283 | " |
| 240 | -196 | 74.2 | 83.1 | 119.1 | 42.5 | 287 | " |
| 240 | -196 | 74.4 | 82.6 | 117.2 | 36.5 | 283 | " |
| 960 | -196 | 72.7 | 80.8 | 113.0 | 32.7 | 283 | " |
| 3,840 | -196 | 71.7 | 79.9 | 117.0 | 39.5 | 283 | " |
| 3,840 | -196 | 72.5 | 80.7 | 110.6 | 31.5 | 287 | " |
| 15,360 | -196 | 71.1 | 79.2 | 100.5 | 22.0 | 283 | Intergranular |
| 15,360 | -196 | 70.6 | 78.7 | 112.0 | 36.5 | 276 | Slight shear; fine system of cracks. Flat transverse |
| 30,000 | -196 | 68.7 | 76.0 | 119.0 | 40.4 | 269 | " |
| 30,000 | -196 | 71.5 | 78.8 | 106.5 | 36.0 | 272 | " |
| 30,000 | +20 | 42.9 | 51.7 | 102.0 | 63.0 | 271 | Well developed cup and cone, with some radial fissures |

All stresses in tons/sq.in. Hardness measured with 10 Kg.load

longest embrittling time used (500 hrs.). This may be due to "overaging" as reported by Vidal[18], but the effect in this case could be spurious.

The load extension curves of these steels showed a maximum, without exception, and all specimens showed a local reduction of area. The slight fall in U.T.S. and Yield Stress after long embrittling times was probably due to slight softening of the material.

The fall in ductility of the 'tough' material by changing the testing temperature from 20°C to -196°C (66-47.5%), was much less than for the coarse grained material, but the increase in yield stress and U.T.S. was virtually the same as for that material. The appearance of the low temperature fracture was quite different. Figs. 39 and 40 show the room temperature and low temperature fractures of this steel respectively. Here, the low temperature fracture showed some shear at the peripheral region of the specimen. The major portion of the fracture had a quite distinctive appearance, but was neither intergranular nor similar to the fibrous parts of the more ductile fractures. Most of the steels in this series gave this flat transverse failure, with more or less shear, depending on the ductility. One of the highly embrittled specimens with 22% reduction of area, gave a recognisably intergranular

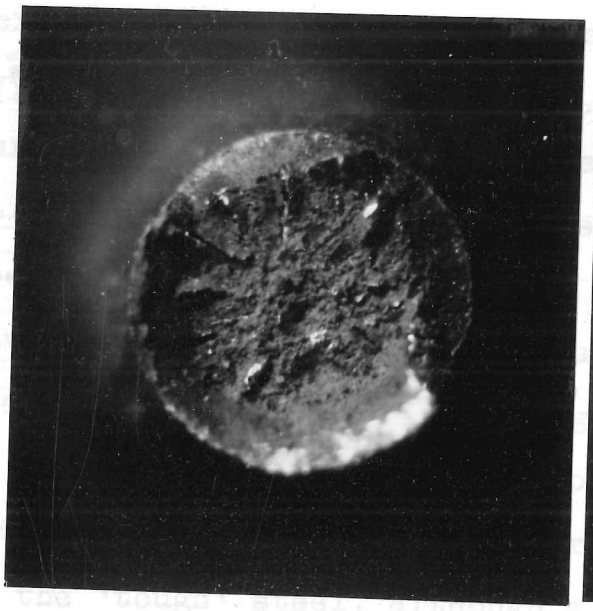


Fig. 39 x 25

Fig. 40 x 25

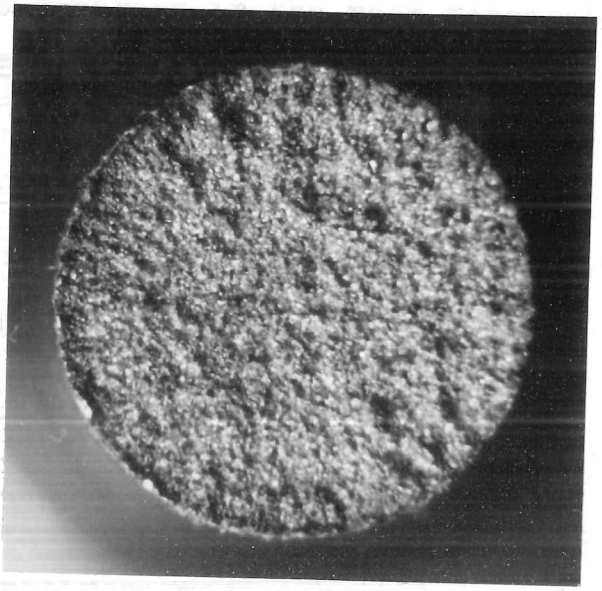


Fig. 41 x 25

fracture (Fig. 41). All the low temperature fractures (except that of the 'tough' steel) were characterised by a system of very fine cracks, present over the whole surface of the fracture. It is thought, from their very fine scale, that these were intergranular, although they could not be identified as such. They seem to have been caused by the tri-axial stresses at the tip of the crack, which was propagating to give the final failure.

The room temperature properties of the steel after 500 hrs. embrittlement were very similar to those of the 'tough' steel, although a slight fall in the reduction of area was apparent (66-63%).

It can be concluded therefore, that the low temperature properties do give some indication of the state of embrittlement of the steel, but that no real effect is apparent in the room temperature properties.

It is also evident from a comparison of the two series that the Yield Stress-Temperature relationship is very little affected by either the amount of embrittlement, or the change in grain size. This justifies one of the assumptions made in Chapter II.

<u>EN 23, 0.021% As, A.S.T.M. Grain Size 1-3</u>. Specimens for treatment were taken from the fractured impact specimens used in obtaining the data given in Table XIII. The 'tough' specimens were embrittled at 525°C for various

Table XVIII

EN 23, 0.021% As, A.S.T.M. Grain Size 1-3

| Time at 525°C (Minutes) | Testing Temp. °C | Yield Stress | U.T.S. | T.F.S. | %R.of A. | D.P.H. | Description of Fracture |
|---|---|---|---|---|---|---|---|
| 0 | +20 | 50.5 | 59.5 | 110.0 | 57 | 286 | Cup and Cone |
| 0 | -196 | 80.7 | 88.8 | 127.4 | 36.7 | 285 | Flat transverse fracture |
| 0 | -196 | 82.1 | 91.1 | 124.7 | 30.2 | 285 | " " " |
| 240 | -196 | 81.3 | 89.1 | 103.1 | 14.1 | 287 | Intergranular |
| 240 | -196 | 83.6 | 92.3 | 111.7 | 19.5 | 287 | " |
| 960 | -196 | 83.8 | 87.9 | 110.5 | 20.5 | 285 | " |
| 960 | -196 | 79.6 | 81.3 | 84.1 | 3.3 | 285 | Fractured at fillet |
| 3,840 | -196 | 83.8 | 86.2 | 93.6 | 9.0 | 282 | Intergranular |
| 3,840 | -196 | 80.4 | 86.8 | 94.9 | 8.5 | 282 | " |
| 15,360 | -196 | 78.4 | 87.3 | 107.5 | 19.6 | 279 | " |
| 15,360 | -196 | 79.6 | 88.3 | 103.5 | 14.7 | 279 | " |
| 60,000 | -196 | 72.5 | 80.7 | 102.8 | 23.0 | 270 | " |
| 60,000 | -196 | 72.1 | 80.3 | 101.2 | 21.5 | 273 | " |
| 60,000 | +20 | 45.6 | 55.0 | - | 55 | 270 | Cup and cone, with radial cracks |

All stresses in tons/sq.in. Hardness measured with 10 Kg.load

times up to 1000 hrs. The results of the tests are recorded in Table XVIII, and they are shown graphically in Fig. 42. Two new effects are immediately apparent from the curves. Both the true fracture stress, and the reduction of area, fall with increasing embrittling time up to about 60 hrs. The U.T.S. also shows a slight fall at this time, indicating specimens that failed without necking. Both the fracture stress and the ductility increase at longer embrittling times. This it seems is almost certainly due to "overageing", i.e. the intergranular brittle strength increases. At the longest embrittling time, the true fracture stress falls again slightly. This is accompanied by a fall in yield stress, U.T.S., and hardness, and therefore must be due to softening.

The fall in ductility of the 'tough' material on changing the testing temperature from 20 to -196°C was similar to that for the coarse grained, high arsenic steel (57-33.5%), indicating that the arsenic had little effect on this property. The room temperature ductility of the steel given the 1000 hr. treatment was almost the same as that for the 'tough' steel, but the yield strength had fallen considerably. The lower susceptibility of this steel in comparison with the high arsenic steel is therefore apparent both in the room temperature properties

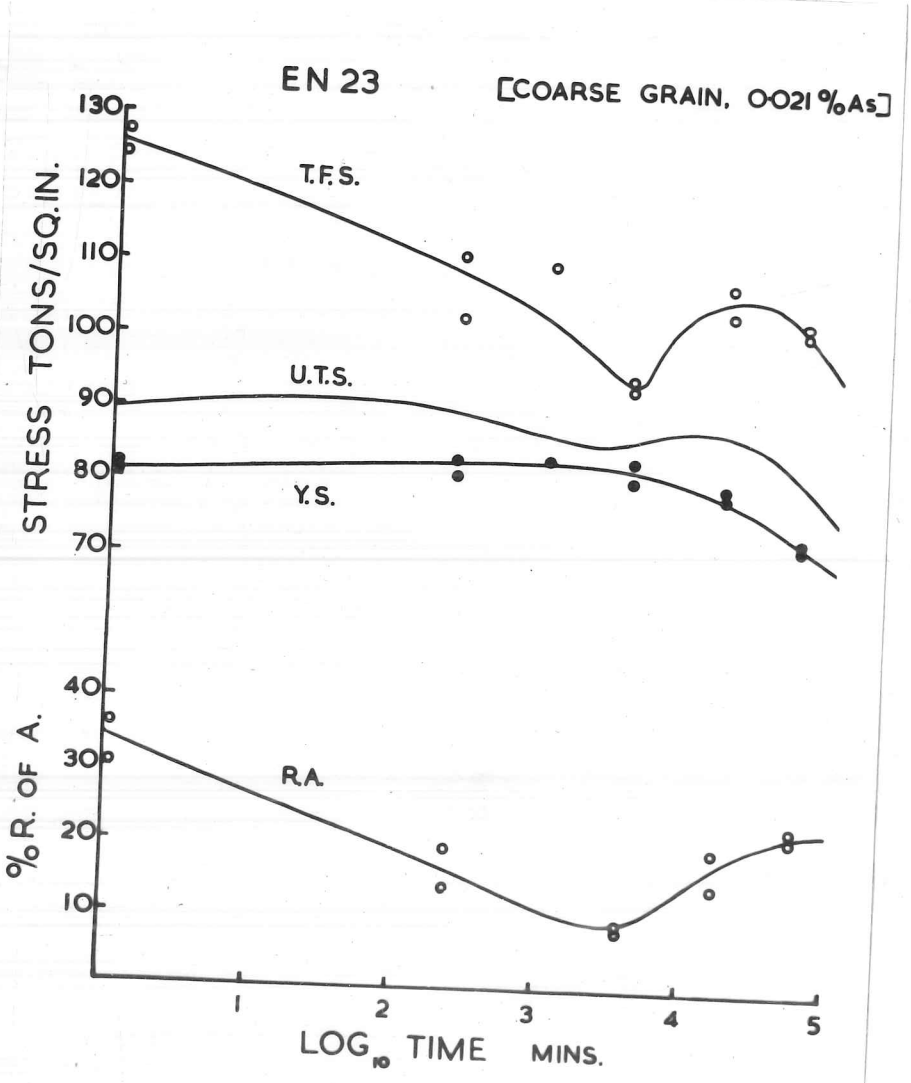

EN 23
[COARSE GRAIN, 0·021 %As]
STRESS TONS/SQ.IN.
130
120
110
100
90
80
70
T.F.S.
U.T.S.
Y.S.
% R. OF A.
40
30
20
10
R.A.
1
2
3
4
5
LOG10 TIME MINS.

Fig. 42

and the properties at -196°C.

EN 23, 0.021% As, A.S.T.M. Grain Size 8-9. Specimens for heat treatment for this series were taken from the impact pieces used in obtaining the data given in Table IV. The 'tough' specimens were embrittled at 525°C for times up to 1000 hrs. The results of the tests are given in Table XIX, and are shown graphically in Fig. 43. It is quite obvious that the tensile properties at -196°C are only very slightly affected by the embrittlement. The fracture stress never fell below 129 tons/sq.in., or the reduction of area below 40%. There is some indication of overageing, but this is only slight. The large drop in fracture stress on the specimen embrittled for 1000 hrs. again reflects the softening of the material.

The drop in the ductility of the 'tough' steel from 20 to -196°C is not large (the reduction of area falls from 68% to 52%), and this latter value regained by the steel after the longest treatment at 525°C.

The low temperature fractures of the steels were all of the same type as that shown in Fig. 40, but generally with more shear fracture at the edge. In no case was any of the fractures identified as intergranular. It may be concluded from these tests that a good quality low alloy steel of the EN 23 type, is unlikely to show

Table XIX

EN 23, 0.021% As, A.S.T.M. Grain Size 8-9

| Time at 525°C (Minutes) | Testing Temp. °C | Yield Stress | U.T.S. | T.F.S. | %R.of A. | D.P.H. | Description of Fracture |
|---|---|---|---|---|---|---|---|
| 0 | +20 | 48.9 | 55.6 | 127.0 | 68 | 280 | Cup and cone |
| 0 | -196 | 76.2 | 82.0 | 142.8 | 52 | 279 | Slight shear; many fine cracks |
| 240 | -196 | 77.2 | 85.4 | 129.8 | 41.2 | 276 | " |
| 240 | -196 | 78.9 | 87.5 | 141.4 | 48 | 274 | " |
| 3,840 | -196 | 76.4 | 84.6 | 136.8 | 45.3 | 275 | " |
| 3,840 | -196 | 77.2 | 85.4 | 135.4 | 45.4 | 272 | " |
| 15,360 | -196 | 74.2 | 82.3 | 141.5 | 48.2 | 271 | " |
| 15,360 | -196 | 76.4 | 85.0 | 141.5 | 50.1 | 273 | " |
| 60,000 | -196 | 72.0 | 77.9 | 124 | 48 | 264 | " |
| 60,000 | -196 | 71.7 | 78.2 | 112 | 38 | 264 | Fractured at fillet |
| 60,000 | +20 | 46.1 | 53.2 | 122 | 64 | 260 | Cup and cone, with a few radial fissures |

All stresses in tons/sq.in. Hardness measured with 10 Kg.load

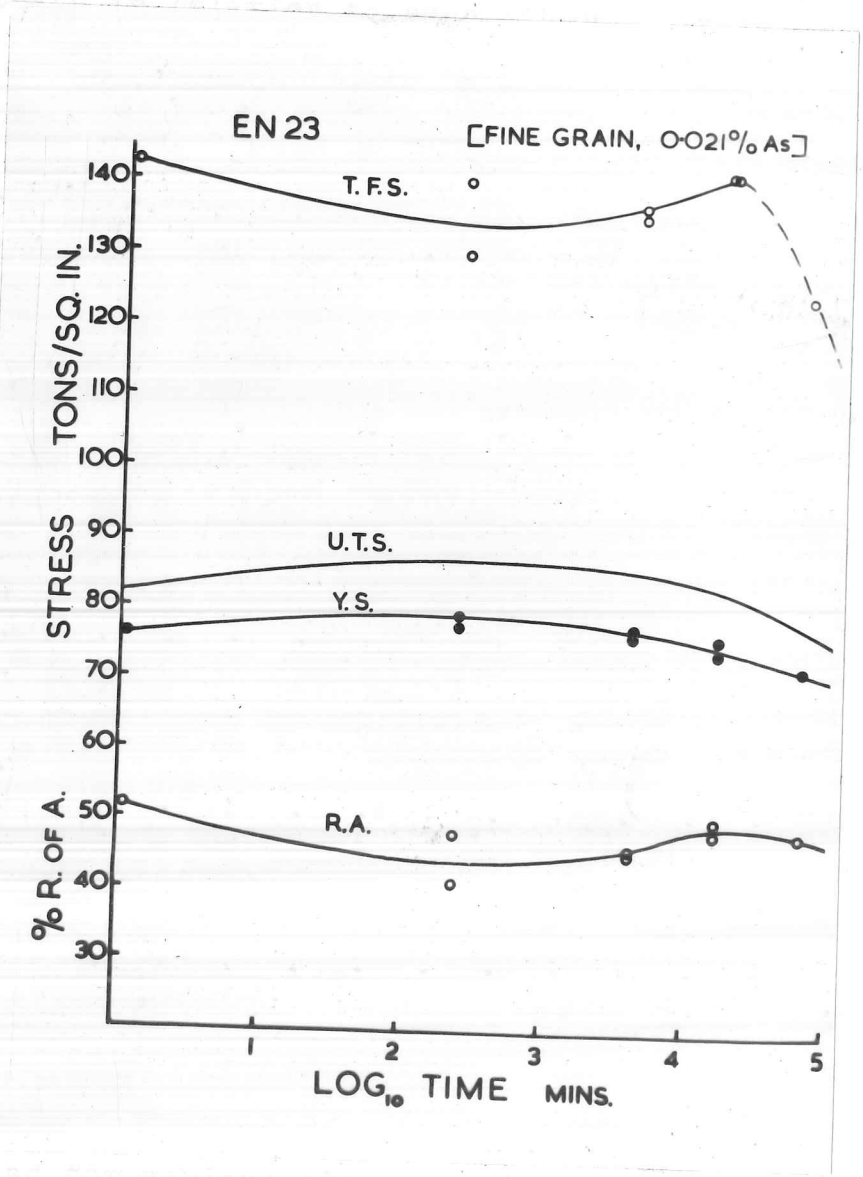

EN 23
[FINE GRAIN, 0·021% As]
T.F.S.
U.T.S.
Y.S.
R.A.
STRESS TONS/SQ. IN.
% R. OF A.
140
130
120
110
100
90
80
70
60
50
40
30
1
2
3
4
5
LOG10 TIME MINS.

Fig. 43

any marked changes in ductility in uniaxial tension at -196°C, due to temper brittleness, provided that the steel is fully heat treated.

It is now possible to consider the four series of tests in relation to each other. It is evident that the austenitic grain size is a more important factor than the amount of arsenic present, in controlling the low temperature ductility, both in the 'tough' and 'brittle' conditions. The effect of an embrittling treatment depends on the ductility in the 'tough' condition; when this is low, extreme brittleness can result from quite short embrittling times; when this ductility is high, temper embrittlement has little effect on the low temperature ductility.

It is also noticeable that the reproducibility of the results is better for the steels with low arsenic. It is possible that the scatter in the values for the steels with 0.255% As is due to segregation of arsenic in the metal.

EN 23, 0.085% Sb, A.S.T.M. Grain Size 7. Specimens for heat treatment were taken from the impact test pieces referred to in Table X. The 'tough' specimens were embrittled for various times up to 240 minutes, in a salt bath.

The results are given in Table XX, and are shown

Table XX

EN 23, 0.088% Sb, A.S.T.M. Grain Size 7

| Time at 525°C (Minutes) | Testing Temp. °C | Yield Stress | U.T.S. | T.F.S. | %R. of A. | D.P.H. | Description of Fracture |
|---|---|---|---|---|---|---|---|
| 0 | +20 | 51.7 | 60.6 | 105.3 | 52 | 295 | Cup and cone, slight radial cracking |
| 0 | -196 | 76.6 | 84.8 | 111.2 | 25.3 | 295 | Intergranular? Fine system of cracks |
| 0 | -196 | 77.0 | 85.2 | 116.4 | 31.3 | 296 | " |
| 10 | -196 | 77.8 | 83.5 | 91.3 | 9.5 | 297 | Intergranular |
| 10 | -196 | 76.1 | 73.5 | 95.6 | 13.0 | 297 | " |
| 30 | -196 | 78.3 | 79.1 | 82.0 | 4.2 | 301 | " |
| 30 | -196 | 78.3 | 79.5 | 82.6 | 4.5 | 302 | " |
| 90 | -196 | 76.7 | 77.1 | 80.0 | 4.3 | 302 | " |
| 90 | -196 | 78.6 | 78.6 | 80.3 | 2.3 | 303 | " |
| 240 | -196 | 78.6 | 77.3 | 78.8 | 1.7 | 301 | " |
| 240 | -196 | 78.3 | 77.5 | 79.3 | 2.2 | 300 | " |
| 240 | +20 | 52.3 | 60.7 | 72.3 | 17.2 | 301 | " |

graphically in Fig. 44.

The treatment at 525°C resulted in extreme brittleness after 100 mins. The true fracture strength fell to 80 tons/sq.in., and the reduction of area to nearly 1%. A new effect is also evident. The yield stress and the hardness show slight but definite increases as the amount of embrittlement increases. The fall in ductility is precipitous, the reduction of area being halved by a 10 minute treatment at 525°C, and the strength of the material falls by 20%

All the low temperature fractures, except those of the 'tough' steel, were found to be intergranular, and the steel given a 4 hour embrittlement, showed an intergranular fracture at room temperature. There is no doubt that both the room temperature and the low temperature tensile properties as well as hardness give clear indications of the embrittlement. Temper embrittlement, can therefore, be detected by the usual mechanical tests when sufficiently severe, as for the more well known phenomenon of age hardening, and euctoid transformation.

An attempt was made to assess the effect of strain on the brittle strength of this steel. A specimen which had been embrittled 240 mins. at 525°C, was strained at room temperature to 4.5% reduction of area. This strained

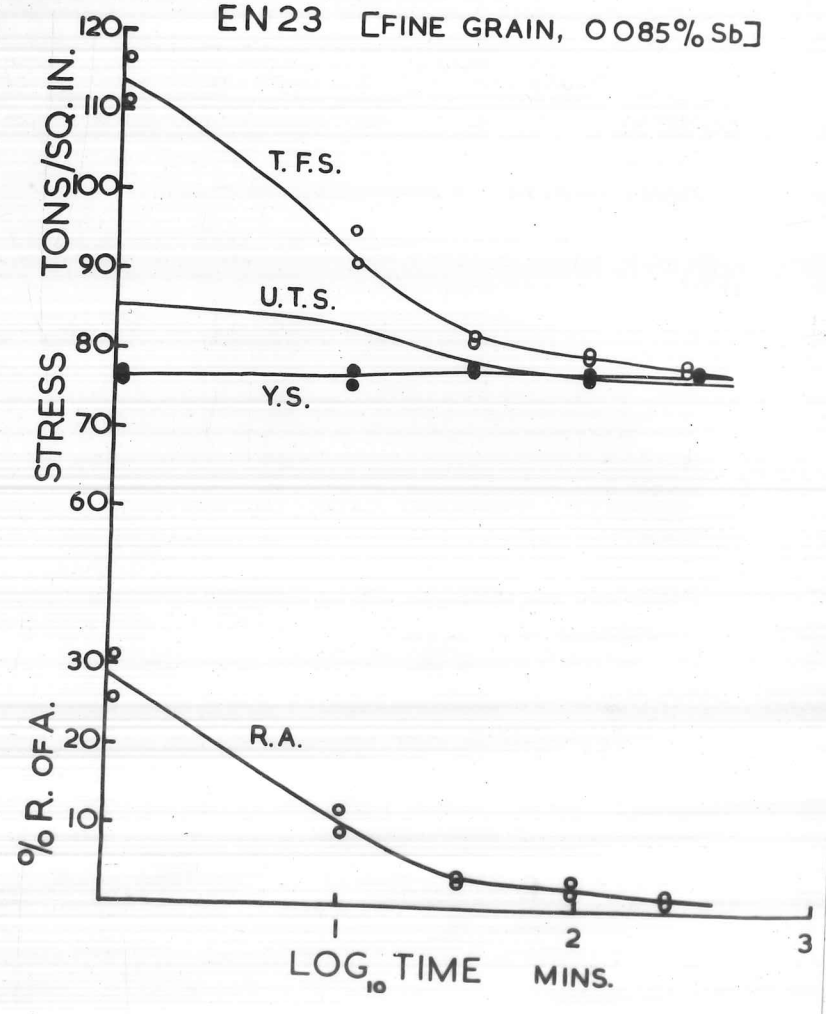

EN 23 [FINE GRAIN, 0·085% Sb]
STRESS TONS/SQ. IN.
120
110
100
90
80
70
60
T.F.S.
U.T.S.
Y.S.
% R. OF A.
30
20
10
R.A.
1
2
3
LOG10 TIME MINS.

Fig. 44

test piece was then strained further at -196°C until fracture. A further reduction of area of 1.3 (on the original area) took place, and fracture took place at a stress of 84.2 tons/sq.in. Together with the two results already obtained for this material, it was found by extrapolation that the brittle strength at 0% deformation was 76.5 tons/sq.in., this being raised 1.3 tons/sq.in. by each 1% reduction of area.

Although the utility of this type of determination is still problematical , it is proposed to apply this correction for small deformations, where required.

Relation Between Tensile and Notched Bar Properties.

From the data given in Tables XVI to XX, it is now possible to calculate the relationship between the transition temperature in the notched bar test, and the brittle strength.

Using the notation applied in Chapter 2, we have

$$\text{Yield Stress} = Ae^{-BT}$$

Table XXI gives the values of A and 1/B calculated for the different steels tested.

It is seen that 1/B is fairly constant, except for the first and last steels in the table. These two high values are probably due to the greater hardness of these steels. The results of Ripling(69) for a 1.8% Mn

Table XXI

| Designation | (A) | (1/B) | D.P.H. |
|---|---|---|---|
| EN 23, 0.255% As, C.G. | 91.0 | 503 | 297 |
| EN 23, 0.255% As, F.G. | 86.4 | 465 | 284 |
| EN 23, 0.021% As, C.G. | 96.5 | 452.5 | 285 |
| EN 23, 0.021% As, F.G. | 90.6 | 463 | 278 |
| EN 23, 0.088% Sb, F.G. | 90 | 545 | 295 |

steel show that as the tempering temperature is increased from 600 to 1100°F, 1/B changes from 778 to 509. It seems a general principal, that the value of 1/B decreases with hardness. The value of A, (which is numerically equal to the value of the yield stress extrapolated to 0° absolute), does not vary greatly.

Now,

$$\text{Transition Temperature} = \frac{1}{B} \ln \left(\frac{kA}{C}\right)$$

Where C is the brittle strength.

For EN 23, 0.255% As, (coarse grained) embrittled 250 hrs. at 525°C, the brittle strength is 78 tons, and the transition temperature 230°C., and therefore k = 2.4.

This means that the effective value of the stress

concentration factor for the Izod test is 2.4. With this value of k it is possible to calculate the brittle strengths corresponding to the transition temperatures previously determined. These values are given in Table XXII overleaf.

From the values of $\Delta_{BS}$ it is seen that the differences in susceptibilities of the steels, and the differences in the 'tough' transition temperatures, are in fact due to changes in brittle strength, and not due to the effect of the arsenic on the plastic properties of the metal. When considered from this point of view, i.e. the effect of the transformation on the brittle strength, it is evident that quite large changes in brittle strength take place, due to temper embrittlement, which are comparable in magnitude with strength changes associated with age hardening systems. It must be assumed that it is only the very localised nature of the precipitation, which usually prevents any marked changes in the room temperature properties.

The calculated value of k, is less than that assumed in the analysis given in Chapter 2, but this only makes slight differences in some of the quantitative predictions. For example, it was assumed that the difference in transition temperature between tensile and impact tests was numerically equal to 1/B. With k = 2.4, this

Table XXII

| Steel | Grain Size | $T_a$ | $C_a$ | $T_b$ | $C_b$ | $T'_b$ | $C'_b$ | $\Delta C$ | $\Delta T$ |
|---|---|---|---|---|---|---|---|---|---|
| EN 23, 0.255%As | 1-3 | +30 | 119.6 | +206 | 82.4 | +230 | 78 | 37.2 | 170 |
| EN 23, 0.255%As | 7-8 | -78 | 136.4 | +46 | 104.5 | - | - | 31.9 | 124 |
| EN 23, 0.022%As | 1-3 | -86 | 149 | +34 | 112.6 | +46 | 109.4 | 36.4 | 120 |
| EN 23, 0.022%As | 8-9 | -112 | 153.6 | -42 | 126.1 | - | - | 27.5 | 70 |
| EN 23, 0.088%Sb | 7-8 | -24 | 133.8 | +293 | 76.5 | - | - | 57.2 | 317 |

$C_a$, and $C_b$, are the 'tough' and 'brittle' strengths respectively (tons/sq.in.). $\Delta C$ is the difference $C_a - C_b$. $T_a$, and $T_b$, are the 'tough' and 'brittle' transition temperatures respectively. ($^oC$.) $\Delta T$ is the difference $T_a - T_b$. T' refers to the steels embrittled for 250 hours. The value of $T_b$ for the steel containing antimony is calculated on the assumption that the brittle strength is 76.5 tons/sq.in.

must be modified to $\frac{0.875}{B}$. This lies between 395 and 475°C for the steels tested.

It must be realised that in tension tests, a 25% drop in ductility (or energy absorption) occurs by a different mechanism than in notched bar impact tests. In tension, if the brittle strength is greater than the yield stress, then deformation takes place. This raises the brittle strength and the yield stress, but the latter to a greater degree. Fracture occurs when they become equal. The transition in tension, for temper brittle steels, takes place by a decrease in the overall ductility. The mechanical factors influencing the initial reduction in ductility, where the fracture is not intergranular, are not understood, and can be compared to with a similar transition from ductile to cleavage failure which occurs in mild steel, when tested under similar conditions. In the impact test, the transition takes place by changes in the relative amounts of ductile and brittle fracture. For comparison between the two tests, it appears that the temperature at which complete brittleness in tension occurs, should be compared with the temperature at which brittle facets appear in the notched bar test. In this case, the predicted values lie near the experimental values (e.g. for the steel first listed in Table XXII, the predicted value is 440, and the experimental value

is 426°C). From this it is also seen that complete brittleness in tension can not be expected for the steels under consideration, unless the transition temperature (notched bar impact) exceeds 200-280°C, depending on the particular steel dealt with; this is in accordance with the experimental results. To produce an appreciable fall in the ductility (25%), it appears to be necessary to increase the transition temperature (notched bar impact), to room temperature or slightly above. This is in striking contrast to mild steels, for which a steel with a transition temperature near room temperature is completely brittle in tension at -196°C.

Conclusions.

(1) The ductility of 'tough' steels at -196°C depends on both the austenitic grain size, and the arsenic content. The grain size is the more important factor in the steels studied. It appears to be a function of the transition temperature in a notched bar test. The yield point is very marked at the low temperature.

(2) The effect of the embrittlement at 525°C on the low temperature properties depends on the susceptibility of the steel, and on its initial condition. When the embrittlement is sufficiently severe, the general elongation is partly suppressed, and in its most marked form, failure occurs at the yield point. The retained

ductility of the steel appears to correlate roughly with the notched bar transition temperature.

(3) When failure occurs with low ductility (less than 20% R.A.), the fracture becomes recognisably intergranular. Steels with greater ductility show a flat transverse type of fracture, but in general do not appear to be intergranular.

(4) When embrittlement is sufficiently severe, the mechanical properties, and the appearance of the fracture, give clear indications of the embrittlement.

(5) Fine grained, quenched and tempered steels, containing low phosphorus, arsenic, and antimony, show only slight reductions in ductility at -196°C, due to embrittlement.

(6) After very long embrittling times at 525°C, the ductility and the fracture stress of the steels are somewhat restored. This supports the evidence of Vidal, that "overageing" takes place when the embrittling treatment is sufficiently prolonged.

(7) The correlation between low temperature tensile and notched bar tests, is sufficiently good to be useful in interpreting experimental data, but the theory developed previously, can only be regarded as approximate.

(8) The phenomenon of temper brittleness can be regarded as a manifestation of the lowering of the grain boundary cohesion (intergranular brittle strength) due

to a segregation or precipitation at the prior austenite grain boundaries.

# CHAPTER VIII

## METALLOGRAPHY.

This chapter contains accounts of various experiments, all directed at elucidating the mechanism of temper brittleness, but not necessarily connected with the work already described.

### Introduction.

Cohen, Ulrich and Jacobsen[20] and McLean and Northcott[21] developed etching reagents which attacked the austenitic grain boundaries of temper brittle steels. They found that if a surface active reagent (detergent) was added to a 10% solution of picric acid in ether, satisfactory delineation of the grain boundaries could be achieved. The most potent compounds were Zephiran Chloride (alkyl-dimethyl-benzyl ammonium chloride), Aryl E.P.G. (aryl ether of polyethylene glycol), and C.T.A.B., (cetyl-trimethyl ammonium bromide).

Although they found that some grain boundary attack took place in 'tough' steels, adequate discrimination could be made.

### Structures of Specimens Used in Impact Tests.

In the experiments described here, the solution used contained 1% C.T.A.B. All references will be made

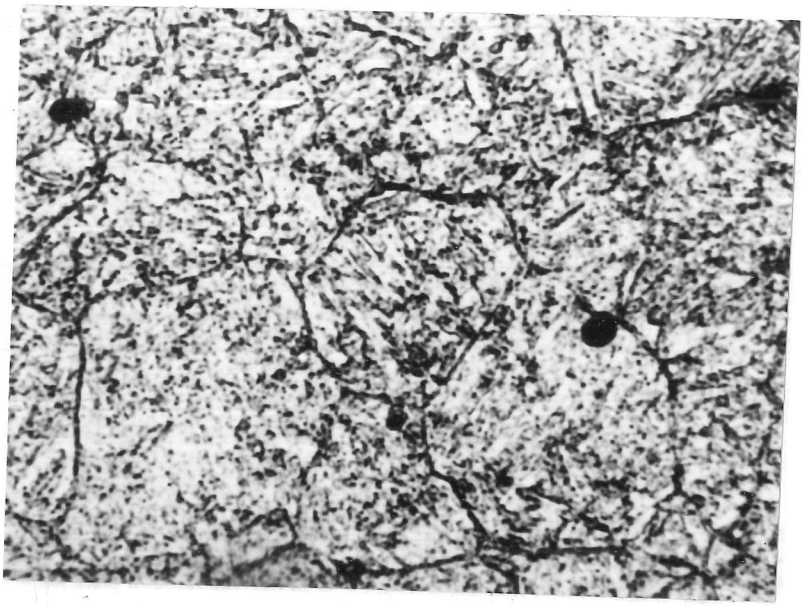


Fig. 45 x 1000

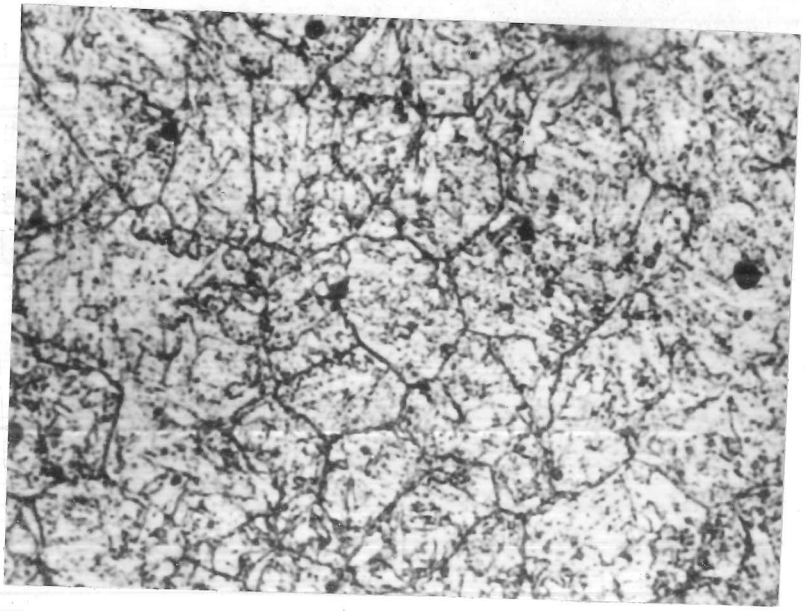


Fig. 46 x 1000

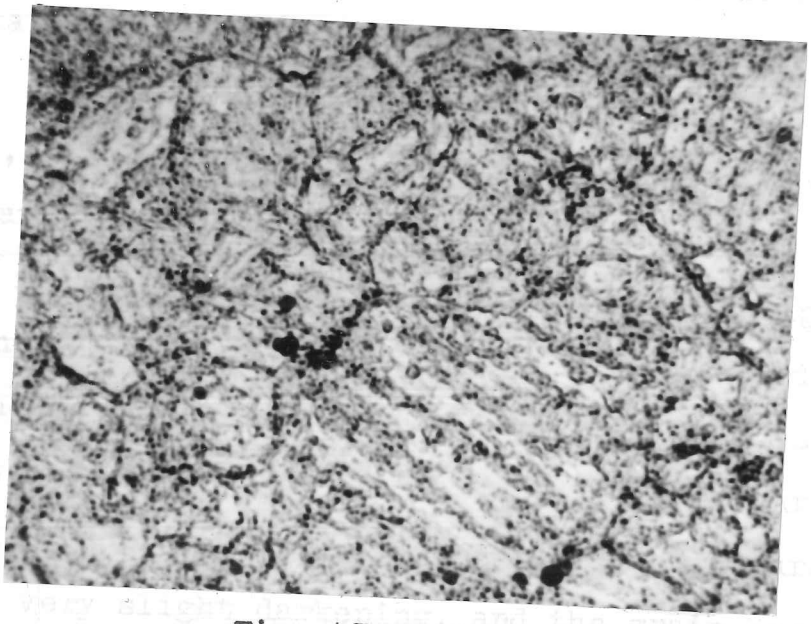


Fig. 47 x 1000

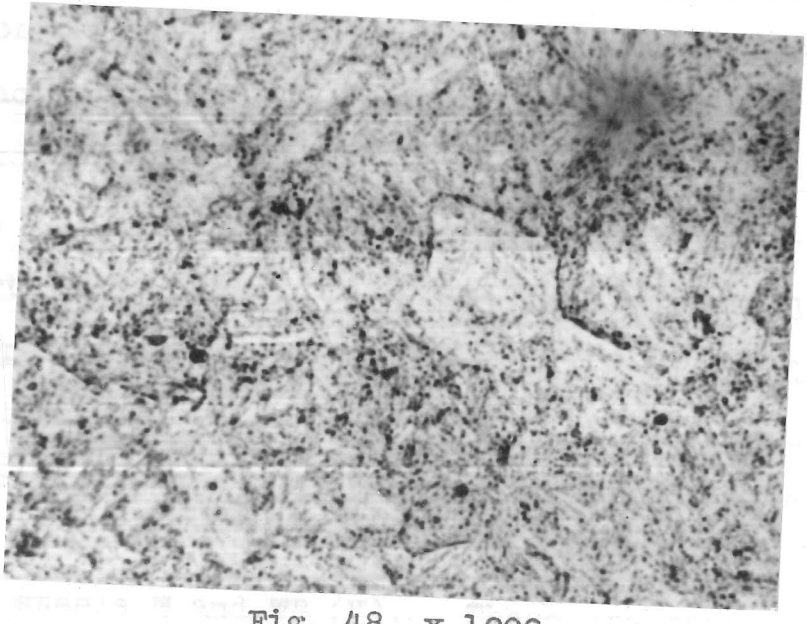


Fig. 48 x 1000

to the table containing the necessary heat treatment data, with the identification letters.

Fig. 45 shows the structure of steel VB (Table IV), etched with C.T.A.B. The grain boundaries are clearly shown. Fig. 46 shows steel SB (IV) in which the finer austenitic grain size, and the slightly less pronounced grain boundary attack correlate with the impact properties. Fig. 47 shows the same steel S (IV) in the 'tough' condition. Here, the boundaries although visible, are not well defined. There appears to be only very slight darkening, and the grain boundary carbides, which are clearly shown up, contribute greatly to the definition.

The presence of etching effects at the austenite grain boundaries cannot be regarded as a certain indication of whether the steel is 'tough' or 'brittle' by the fracture criterion described in Chapter V. It seems likely that the grain boundary attack does indicate the presence of precipitate, for it is clear that a certain minimum amount of precipitation will be required to produce an intergranular fracture. If less than this amount is present, intergranular fracture will not take place, although etching effects will be expected.

This is further borne out by the structures of the steels W and WB (V). These are shown in Figs. 48

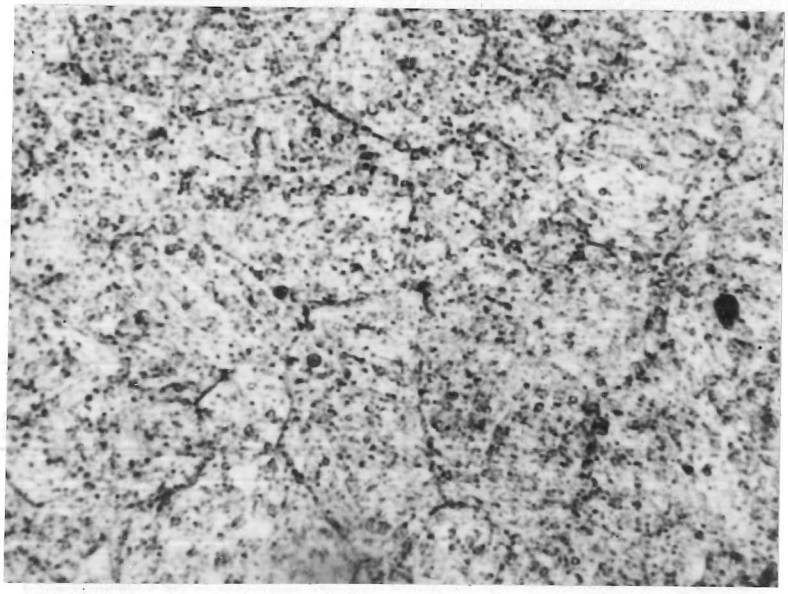


Fig. 49 x 1000

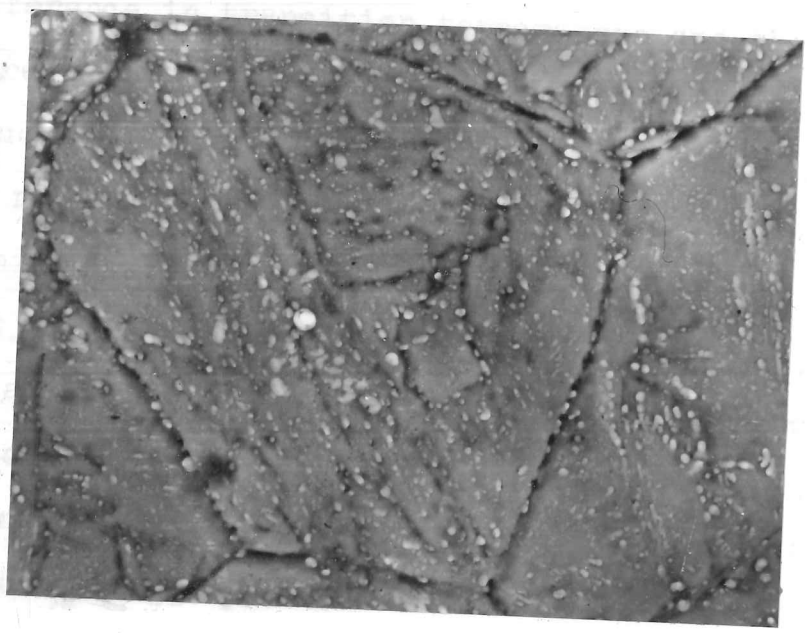


Fig. 50 x 5000

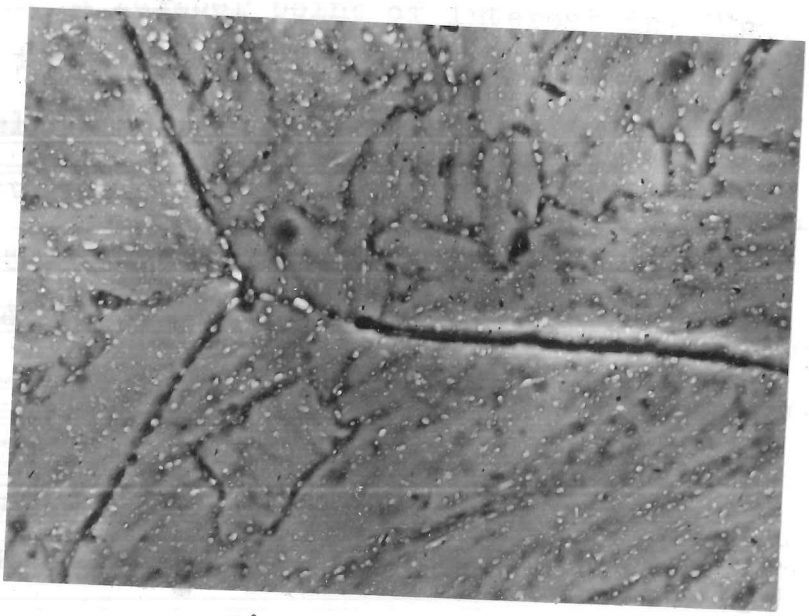


Fig. 51 x 5000

and 49 respectively. There is no doubt that the difference in transition temperature and the low temperature fracture between W and WB is accompanied by microstructural changes. The grain boundaries in Fig. 49 are more distinct than in Fig. 47, and are hardly discernible in Fig. 48. These three specimens must represent three different stages of precipitation, even though two are 'tough', and give substantially cleavage fractures at low temperatures. The fact that a very small number of intergranular facets were present in the 'tough' fractures supports this view. It must also be remembered that Fig. 23 gives definite evidence that embrittlement can take place at all temperatures up to $Ac_1$ in coarse grained steels, and presumably takes place (to a lesser extent) in fine grained steels.

A further point of interest in Figs. 45-49 is the internal structure of the grains. The 'brittle' steels show traces of sub-boundaries. Fig. 50 is an electron micrograph of a steel in the 'brittle' condition. The grain boundary attack is pronounced, and the sub-boundaries are clearly shown. Carbide particles are seen to be unattacked, both in the grain boundaries and elsewhere. These sub-boundaries may correspond with the areas of martensite of the same orientation. The etching effects at them do not depend solely on the

difference in orientation across the boundary, since this type of attack does not occur in 'tough' steels. It must be concluded that precipitation occurs both at the prior austenitic grain boundaries, and at certain sites within the grains.

The substructure is clearly shown in Fig. 51, and it can also be seen that there is no sign of discreet particles in the grain boundaries, other than the normal carbides, which are left unattacked. These electron micrographs prove also that the dark appearance of the austenite grain boundaries in the optical micrographs is due to the removal of material from the boundaries. This is in contrast to the dark appearance of the carbides, which are left raised above the general surface level; in this case, the visual aspect is controlled by the small size of the particles. McLean and Northcott were unable to distinguish discrete precipitate particles, even in specimens embrittled for three months at 500°C, i.e. they found no evidence of spherodization.

An attempt has been made to observe the particles of precipitate, by extracting them electrolytically from the surface of a temper brittle fracture, and then examining them at a high magnification on the electron microscope. The technique adopted is described briefly below.

The low temperature fracture of a severely

embrittled steel (EN 23, 0.255% As, A.S.T.M. Grain Size 1-3, 250 hrs. at 525°C, after quenching and tempering), was anodically dissolved in 10% HCl for sufficient time to dissolve a layer 1000 Å thick off the surface. (5 mins. at 12 mA.) The undissolved carbides, and other matter, adhered to the surface as a dark grey sludge. The fracture was then carefully washed and dried. A few drops of a 3% solution of Formvar in dioxane, were applied to the surface, and allowed to dry. The specimen was immersed in water, and the Formvar film, with the undissolved matter adhering to it, was stripped off. It was washed in alcohol, and dried. The film was then dissolved in chloroform, and the suspension was poured out over glass microscope slides. The films formed on these slides were cut into small squares, removed by immersion in water, and floated onto copper grids, for examination. The films were dried off in a dessicator.

By using this technique, it was hoped to avoid the loss of very small particles, which occurs when the more conventional extraction methods are used. These losses can occur in two ways, (1) the particles may dissolve in the HCl, when kept in contact with it for any length of time. (2) the small particles may be kept in suspension in the liquid, due to Brownian motion,

and so not be collected with the other matter.

Particles were also extracted from etched micro-sections, for comparison with those from the fracture.

When examined at x 10,000 no appreciable differences could be detected between the two sets of particles, other than the greater average size of those from the fracture. This was to be expected, because of the larger carbides at the austenite grain boundaries. There appeared to be no particles of distinctive shape (needles, plates etc.) amongst those from the fracture surface.

This negative result may have been due to the failure of the technique to ensure the collection of the smallest particles, or possibly the precipitate dissolved in the anodic treatment at the beginning of the process.

It is only possible to conclude, that this technique failed to show the presence of discrete precipitate particles other than the normal carbide particles, in the material extracted from the surface of a temper brittle fracture.

Banded Structures.

During the examination of a longitudinal section of steel T (0.08% As, coarse grained, severely embrittled) it was found that banding was present, and that the austenite grain size was finer in the light etching bands.

Fig. 52 shows the structure of this steel (etched in C.T.A.B.), where the effect is quite prominent. It was all found to be present in the fine grained steels, but not as pronounced. Fig. 53 shows the steel SB (IV). In the coarser grained band in the centre of the photograph the austenite grain boundaries are less clearly delineated, than in the darker bands. It seemed desirable to determine what segregations were associated with these bands.

Stead's reagent was applied to a longitudinal section of steel VB (IV). This reagent detects segregations of phosphorus and arsenic. Areas which are high in these elements are attacked less rapidly than the rest of the specimen. Copper, which is deposited where the iron is taken into solution by the action of the acid, deposits most on areas low in the impurities mentioned. The regions high in phosphorus and arsenic, are left unattacked, and free from the deposit of copper. Fig. 54 shows an area of the steel, after etching in C.T.A.B. Fig. 55 shows the same area, after further treatment with Stead's reagent for two minutes.

The correspondence between the deposited copper and the microstructural details revealed by C.T.A.B. is very exact. The light etching, coarse grained bands are heavily obscured by copper. The dark etching, fine grained

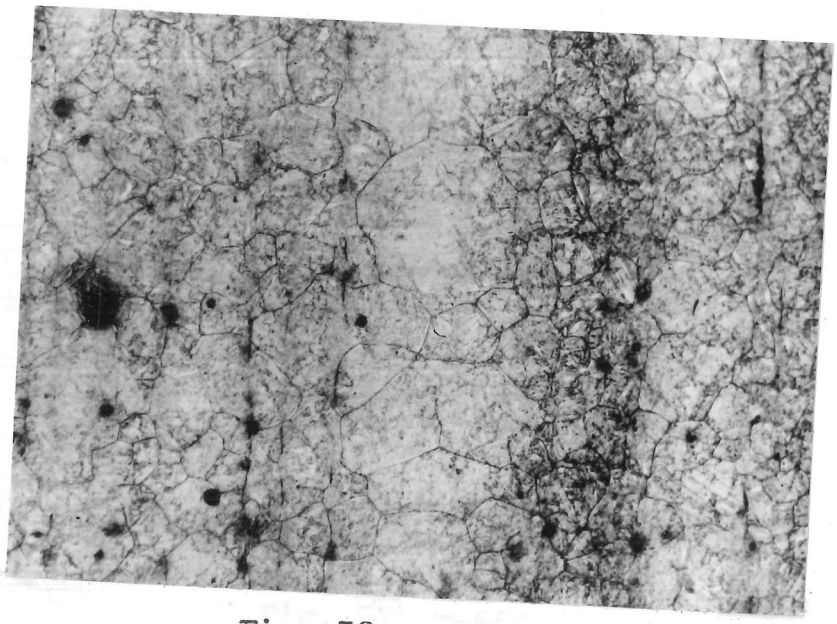


Fig. 52 x 120

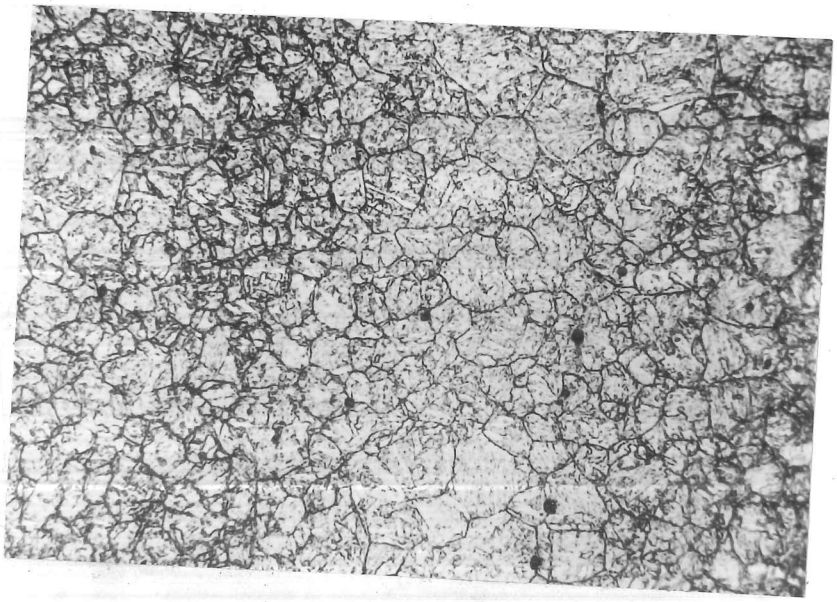


Fig. 53 x 650

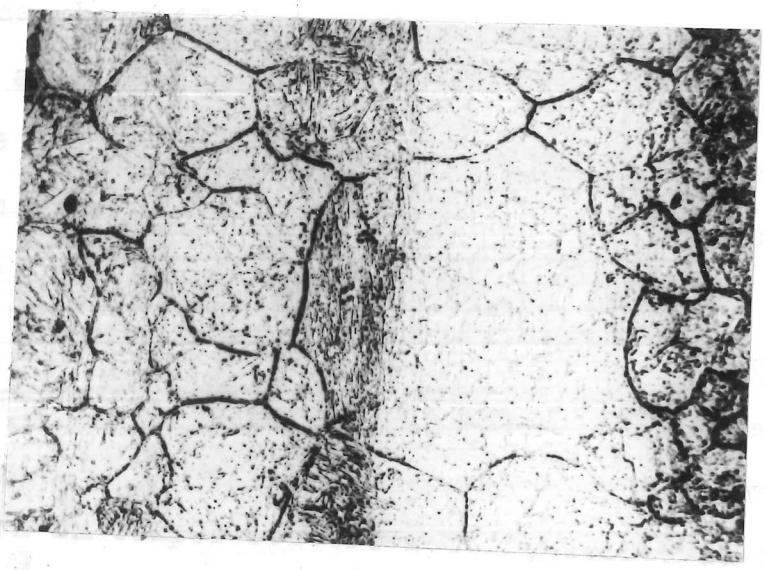


Fig. 54 x 650

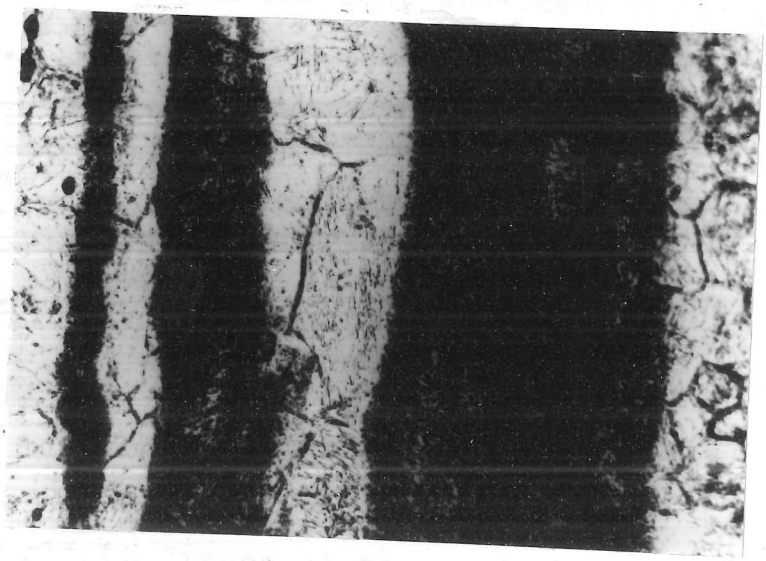


Fig. 55 x 650

bands, are left unaffected, and it follows, that it is these bands which are high in phosphorus and arsenic. It can be said that regions of the metal high in phosphorus and arsenic, and consequently low in carbon, show much more distinct grain boundary attack than other regions, when etched in C.T.A.B. These impurity rich areas also have a finer grain size.

This evidence makes it certain that phosphorus and arsenic, besides their effect on the impact properties, are intimately associated with the grain boundary attack in temper brittle steels, etched in C.T.A.B.

Grain Boundary Effects.

(a) At an early stage of the work with C.T.A.B. it was considered necessary to establish that the etching effects, did in fact correlate with impact properties, after more than one heat treatment cycle (below $Ac_1$), i.e. whether the etching effects were reversible.

This was accomplished in the following way:- a sample of EN 23 steel was oil quenched from 900°C, tempered at 630°C and embrittled at 530°C for 9 hours. It was then etched in C.T.A.B and an identifiable area was photographed. The specimen was next heated in vacuo at 630°C for 3 hrs. water quenched, and repolished and etched; the photographed area was examined, and only slight traces of the grain boundaries were found.

When the specimen was further embrittled at 530°C for 9 hours and repolished and etched, the original grain boundaries were found to be prominently displayed, and the same grain structure was identified.

It can be deduced that the etching effects are reversible, and reprecipitation takes place at the same sites as the original precipitation.

(b) It is difficult to obtain evidence of grain boundary segregation. Some experiments are now described, which were directed towards this end.

On this theory, in a quenched specimen (i.e. martensite) of a steel liable to temper brittleness, segregations are present at the prior austenitic grain boundaries. These must take an appreciable time to disperse, even in the absence of temper brittleness. If the steel is rapidly heated into the austenitic range (800°C), there is the possibility that at short austenising times, the segregations from the first treatment will not be dispersed. If this is the case, and the steel is quenched, and subsequently embrittled, then the locations of the old austenite grain boundaries should be distinguishable, as well as the new boundaries.

A series of specimens of steel T (EN 23, 0.88% As) were heated at 1200°C for 1 hr. and oil quenched. Some were then heated to 900°C for varying times up to 30 mins.

in a salt bath, and oil quenched. One was kept without this treatment. The specimens were next tempered at 620°C and embrittled for 24 hrs. at 525°C, followed by slow cooling. The procedure was repeated with intermediate austenising temperatures of 800° and 850°C on the rest of the specimens.

Fig. 56 shows the austenite grain structure without the second austenising, etched in C.T.A.B. Fig. 57 shows this same material but with 2 mins. at 900°C as the intermediate treatment. The grain structure is coarse (compared with the structures shown in Figs. 45 - 49, and there is no clear evidence of the original high temperature treatment. Fig. 58 shows the material with 2 mins. at 800°C. The old boundaries are clearly shown up, but it is noticeable that they do not cross any of the new grains. It appears that the old boundaries are also boundaries in the new system of grains. Precipitation appears to be greater in the old boundaries. Fig. 59 shows the steel after 16 mins. at 800°C. The old boundaries are less well defined, and the new grains, which are beginning to enlarge, appear to grow across the old boundaries. After 120 mins. at 800°C, the traces of the old grains had almost vanished.

At 850°C a similar series of structures were found, but the elimination of the old grain boundaries

er 16 minutes (Fig.60), they

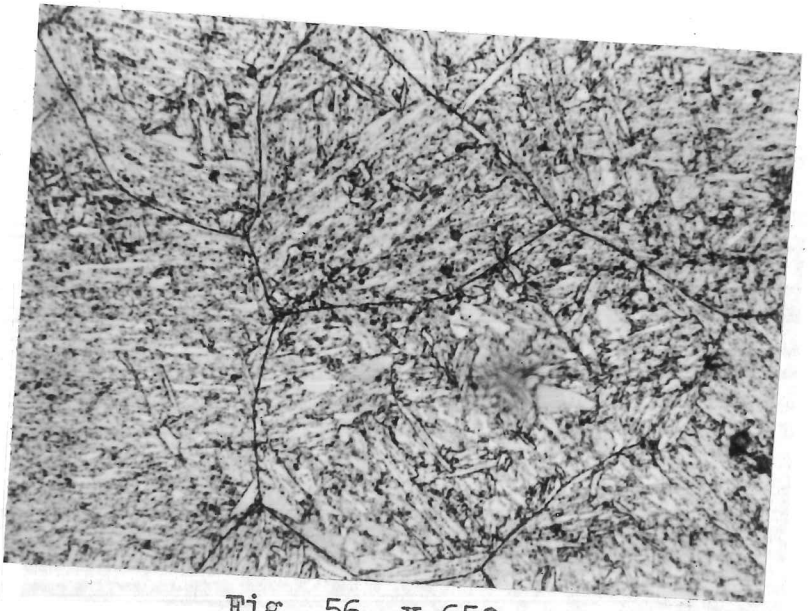


Fig. 56 x 650

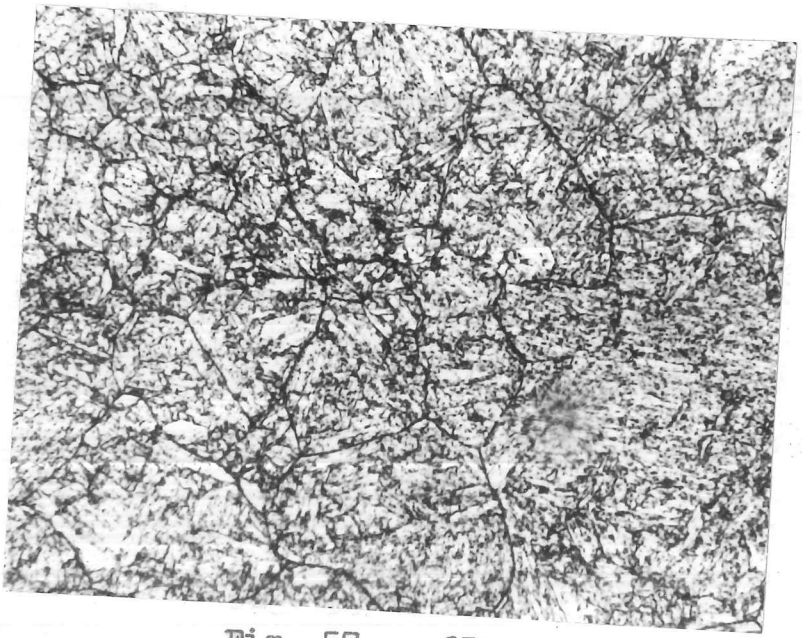


Fig. 57 x 650

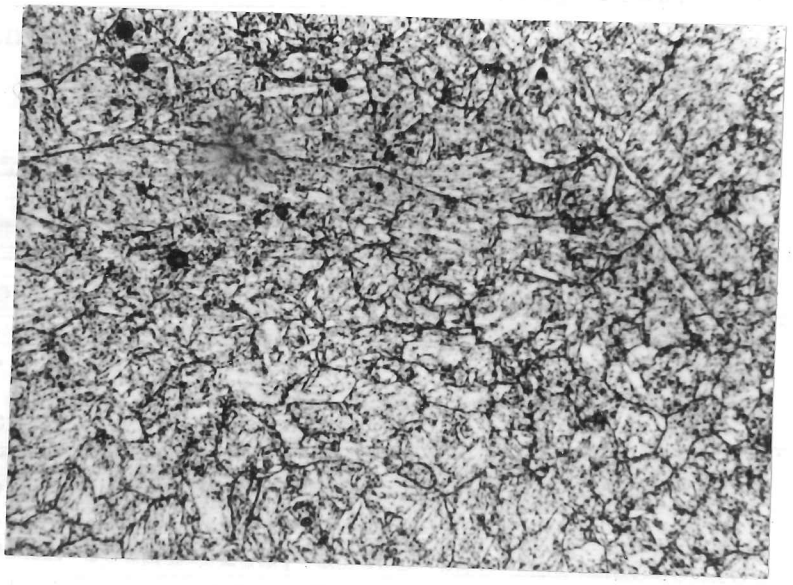


Fig. 58 x 650

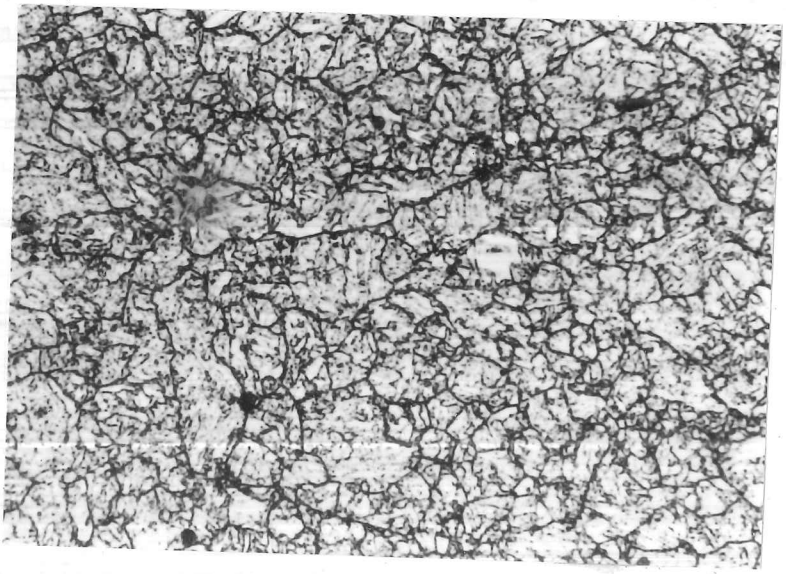


Fig. 59 x 650

are still visible, but have been to a large extent assimilated. After 30 mins. very little trace of them remained. (~~Fig. 60~~)

The process, which at first sight appears to confirm the segregation hypothesis, may be one of grain growth. The new grains may grow up to the old boundaries, but not beyond, until after some time in the austenitic range. This possibility, makes it impossible to conclude with certainty that the observed phenomena are in fact due to grain boundary segregation. This persistance of the grain boundaries, after the new austenising treatment has been reported by Preece, Hartley, and Nutting(68). They found that the sights for the initial precipitation of ferrite from austenite in a EN 39 steel, persisted through more than one austenising treatment, provided the initial heating temperature was high enough. They also showed that the effect persisted through the next austenising treatment, independent of the initial heating temperature.

Conclusions.

(1) The etching effect at the austenite grain boundaries are shown to correlate with the impact properties. No distinct particles of precipitate were observed in the microsections, or in the particles extracted from the

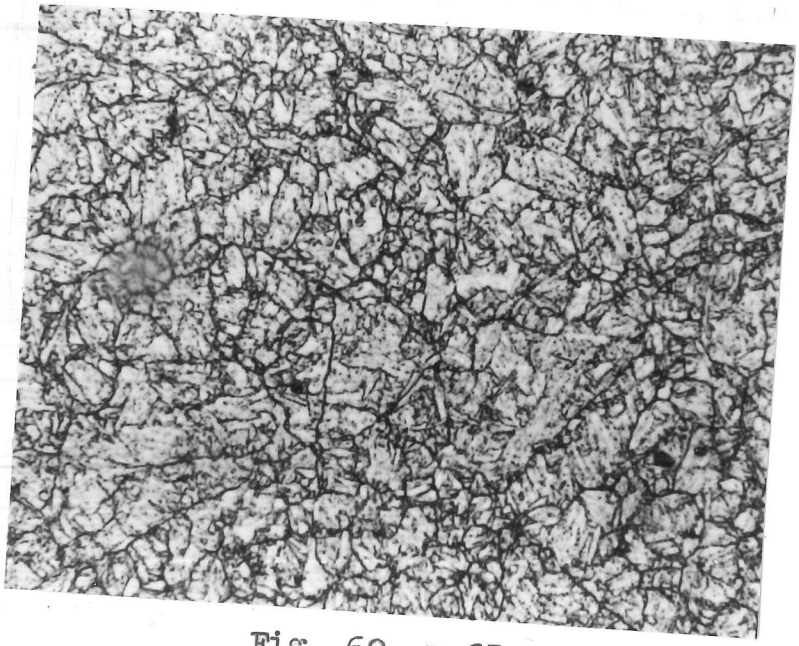


Fig. 60 x 650

fracture surface.

(2) The banding present in the steels is shown to be associated with variations in the austenite grain size. The phosphorus and arsenic rich areas were found to be associated with pronounced grain boundary etching.

(3) The etching effects were found to persist from one austenising treatment to the next, provided the second treatment was at 850°C or less.

# CHAPTER IX

## GENERAL DISCUSSION.

There are three aspects of temper brittleness, which must be elucidated to have a thorough understanding of the phenomenon. (1) The manifestation of the precipitation in the mechanical properties. (2) The mechanism by which the precipitation occurs. (3) The elements which form the precipitate, and its actual composition.

The mechanical aspects of the problem have been discussed at length in Chapters II and VII, and it is thought that these are accounted for satisfactorily. Consideration will now be given to the other two aspects.

The salient features of the phenomenon, which must be explained are:-

(a) Phosphorus, arsenic and antimony, and manganese chromium and nickel, all increase susceptibility to temper brittleness. In the absence of metals of the second group, temper brittleness does not seem to occur, but it appears from very recent work(70) that it can occur in the absence of the elements in the first group. The effect of carbon, is a little obscure. In room temperature tests, very low carbon steels are not susceptible.

(b) Small amounts of molybdenum, added to

susceptible steels greatly reduce the rate of embrittlement, but high molybdenum steels are quite susceptible.(18)(14)

(c) The phenomenon gives rise to intergranular fracture, and pronounced etching effects at the austenite grain boundaries.

(d) Increasing the tempering time gives rise to a reduction of susceptibility, but no prominent change occurs when the tempering temperature is altered.

(e) Embrittlement can occur at all temperatures up to $Ac_1$. Above 550°C, the maximum amount of embrittlement decreases very rapidly. Specimens embrittled at temperatures below 550°C are rapidly restored to their former toughness by heating at temperatures above 600°C.

(f) Embrittlement can take place either by slow cooling after tempering, or by isothermal treatment when the tempering is followed by quenching. The two methods can give rise to comparable displacements of the transition temperature.

(g) No pronounced change occurs in mechanical or physical properties (other than in notched bar tests or low temperature tensile tests), unless the metal is very severely embrittled.

Mechanism of Precipitation.

The great majority of workers on temper brittleness have concluded that the embrittlement is due to the

precipitation of some unspecified phase. There is no direct evidence of the composition of this phase, and only indirect inferences can be made. It has been suggested that either carbon as carbide (iron, or alloy carbides), or phosphorus (alloy phosphides) form the embrittling phase; this is because both these elements affect the embrittlement considerably, and are present in all susceptible steels. In both these cases the influence of the 'hardenability' elements can be visualised, as they all form carbides, or isomorphous phosphides. It is difficult to explain the effect of one element, when the other is assumed to form the precipitate, and the unique effect of molybdenum is also not easily explained.

On any precipitation theory, the effect of grain size, can easily be accounted for, but it is difficult to understand why susceptibility is reduced by long time tempering above 600°C, without making further assumptions. There are three possibilities:- (1) one of the embrittling elements forms an innocuous compound (for example if a chromium compound were the precipitating material, chromium in solution could form $Cr_4C$, and so render the chromium 'non-active'), (2) the precipitation may be dependent on the uneven distribution of an element (or elements) in the metal; long time tempering would lead

to a more uniform distribution, and so reduce the amount of precipitate formed; (3) precipitation occurs at the high temperature, but not in a deleterious form, e.g. it could form as large particles, uniformly distributed throughout the matrix. There is no metallographic evidence that this last process takes place.

The facts that precipitation is reversible, and that it can occur to the same extent by either slow cooling after tempering, or by isothermal treatment when tempering is followed by quenching, are significant. It is here that the temper brittleness phenomenon differs markedly from simple age hardening systems.

On the other hand, the decreasing solid solubility of certain elements in $\alpha$ iron, could explain why embrittlement phenomena take place in the same temperature range in a wide variety of steels.

The intergranular fracture of temper brittle steels is a further phenomenon which requires explanation. It seems unsatisfactory to attribute the location of the precipitate solely to the fact that precipitation occurs at places where the atomic misfit is large (i.e. at the austenite grain boundaries). This also applies to the segregation theory of McLean and Northcott[21]. The austenite grain, does not have a physical existence in quenched and tempered steels, of the type susceptible to

temper brittleness. The effects of its previous existence on the structure have been discussed in Chapter V. It was pointed out there, that the boundaries of the areas of martensite of uniform orientation have similar characteristics to those of the austenite grain boundaries. Precipitation, as judged by etching effects, only occurs to a small extent at these sub-boundaries, and to a much greater extent at the austenitic grain boundaries. It seems necessary to assume that suitable concentrations of elements are already built up at the austenite boundaries, before actual precipitation. These can then give rise to the much greater effects at these sites, when the steel is suitably heat treated.

It is proposed that these segregations are set up whilst the steel is in the austenitic range (prior to hardening), and that certain elements are concentrated to the grain boundaries. These are retained when the steel is quenched, and influence the subsequent behaviour of the metal when it is tempered.

Assuming that precipitation does take place, then this theory explains the location of the precipitate, and the effect of the long time tempering (see above). Further, the 'overageing' reported by Vidal[18], and demonstrated in the low temperature tests in Chapter VII follow on this concept of redistribution of the segregated

material. At the higher temperatures, the solubility of the compound can be assumed to be greater than that at the lower temperatures. In this case, at the higher temperatures, (say above 500°C) the grain boundary can be saturated, and give precipitation, whilst the inner parts of the grain are unsaturated. Diffusion of material can then proceed from the boundary inwards, resulting in re-solution of the precipitate, and a decrease in embrittlement. This mechanism can also apply to the effects occurring in the low temperature fractures of steels tempered at temperature above 600°C (see Chapter V, and particularly Fig. 23). These 'overageing' effects can also be attributed to spherodisation.

The reversibility of embrittlement also follows from the argument given above, provided that 'overageing' has not taken place. In the case where this has occurred, treatment at 600°C and above, followed by embrittling, should give a smaller amount of embrittlement. This has been observed by Jones(9).

The susceptibility of steels depends on the rate of cooling from the austenising temperature. It is thought that in pearlitic steels, the heat treatment gives sufficient time for some of the segregation to be dispersed, and so gives lower susceptibility.

The influence of molybdenum on embrittlement, is

another of the major features of the phenomenon. There is clear evidence that molybdenum decreases the macro-segregation (banding) in manganese steels(69). It is reasonable therefore, to infer that it also tends to disperse the grain boundary segregations. This will result in a reduction of the amount of material available at the grain boundaries for precipitation, and therefore in the rate of embrittlement, but does not necessarily mean that severe embrittlement cannot take place. A further consequence of this dispersion is that the upper limit of the range of temperature in which embrittlement takes place should decrease. At low embrittling temperatures (450°C), where the maximum amount of precipitation can be obtained after extremely long times, it is possible that sufficient can take place, to produce high susceptibility ratios. This does not however, mean that embrittlement takes place to the same extent as that in molybdenum-free steels given the same treatment. This is in agreement with the experiments of Maurer, Wilms and Kiessler(14) whose results show that in most cases, the susceptibility ratios for steels containing molybdenum embrittled 1000 hrs. at 450°C, are less than those of the corresponding steels without molybdenum, which were only slowly cooled after tempering. In all cases which they report, the molybdenum-bearing steels

had a lower susceptibility ratio, when the two types of steels were given the same embrittling treatment. The results also show that molybdenum appears to be more effective in chromium steels than in manganese steels.

The susceptibility of high molybdenum steels can be explained if molybdenum itself, when present in sufficient quantity, can take part in the precipitation in the same way as chromium and manganese.

Nature of the Precipitate.

The composition(s) of the actual precipitate is more obscure than the mechanism of precipitation. It is thought that the elements phosphorus, arsenic, antimony, and possibly nitrogen, act in quite a different way to chromium, manganese, nickel and molybdenum, which are only effective in increasing the susceptibility in much greater quantities. Antimony and phosphorus are much more effective than arsenic, both in promoting temper brittleness, and in increasing the 'tough' transition temperature. This effect may be related to the interatomic distances of these elements. Arsenic (2.51 Å) is nearly the same as iron (2.477 Å); both phosphorus and antimony differ substantially (2.18 and 2.898 Å respectively). Phosphorus and antimony will therefore produce greater distortion of the iron lattice when in solid solution. This may account for the effect on the cleavage

strength, but whether it is significant with regard to the temper embrittlement it is not possible to say.

It was shown in Chapter VIII that phosphorus (and arsenic) were closely associated with the grain boundary etching effects. This does not prove that a phosphide or arsenide is precipitated, but implies that they are closely connected with the precipitation process.

There is no direct evidence available to indicate the actual composition of the precipitate, but it seems likely, from the widespread nature of the phenomenon, and the complexity of the problem, that more than one compound contributes to the observed effects.

Possible Directions for Future Work.

It is evident that the major features of the phenomenon can be explained, but the effects of compositional variables cannot be understood until some direct evidence of the composition is obtained. There are several possibilities in this field, but all of them involve difficult and lengthy techniques.

Micro-radiography, might be used to identify the grain boundary precipitate. The resolving power of the method is not very great, and is probably not sufficient in its present form. Further, it could only be used for study of the heavier metallic elements. Provided the sensitivity can be improved, it seems to be a promising

method of investigation.

Auto-radiography suffers from very similar restrictions. Although it is possible to introduce many of the elements influencing temper brittleness in a suitable radio-active form into a steel, the resolving power of the method depends mainly on the thickness of the sample investigated. There does not appear to be much possibility of reducing this, or the resolving power below 0.001 inches. By using a sensitive radiation detector, it might be possible to distinguish the elements present on the surface of an intergranular fracture. This could be accomplished by comparing the intensity of the radiation from a cleavage and an intergranular fracture of a temper brittle steel. Comparison with the intergranular fracture of untempered martensite, should also decide whether the proposed mechanism is correct.

The examination of particles extracted from the surface of a temper brittle fracture proved unfruitful, but micro-chemical analysis of this material, and also of the solution used in the dissolution, could give an indication of the composition of the precipitate. Here again, the method would have to be used at the limits of its sensitivity.

X-ray, and electron diffraction of the surface

material of a temper brittle fracture is another possible technique. By using glancing angle methods, on the surface of a grain of a very coarse grained steel, it should be possible to detect the precipitate. In conjunction with the other methods outlined, identification of the precipitate seems assured.

All these techniques, would have to be developed to a considerable extent before useful results could be obtained. There is now a great accumulation of experimental data on the manifestation of precipitation, but unless more attention is given to the type of work outlined above, it seems unlikely that the nature of the precipitate(s) will be elucidated, or that the general understanding of the phenomenon will be improved.

Conclusions.

(1) The mechanical manifestation of temper brittleness is now well understood, and the influence of composition and heat treatment on susceptibility is well documented. The work described in this dissertation has shown that:-

(i) Temper brittleness is the manifestation of the lowering of the grain boundary brittle strength.

(ii) Arsenic and antimony increase the transition temperatures of 'tough' steels. It is deduced

that this is due to the lowering of the cleavage strength.

(iii) Arsenic slightly, and antimony very greatly, increase the susceptibility of the steels studied.

(iv) The effects of embrittlement on the tensile properties depends on the severity of embrittlement, and on the temperature of the test. At -196°C embrittled steels have lower ductility, and lower fracture stresses than 'tough' steels, but the effects are only slight in high quality steels, correctly heat treated before embrittlement. (unless antimony is present). With steels containing antimony, the room temperature properties give very definite evidence of embrittlement.

(v) Embrittlement can occur at 620°C, but 'overageing' rapidly takes place. At 525°C 'overageing' occurs, but only after embrittling times greater than 250 hours.

(vi) The presence of intergranular facets in the brittle fractures of the steels investigated, is shown to be a sensitive criterion for temper embrittlement.

(vii) Coarse grained steels are much more susceptible than fine grained steels. The difference in susceptibility can be accounted for by the difference in grain boundary area.

(viii) Increasing the time of tempering (above 600°C) produces a progressive decrease in susceptibility.

(ix) Grain boundary etching effects occur in temper brittle steels, but no evidence was found of discrete particles of precipitate.

(x) The banding present in the steels studied (due to phosphorus and arsenic), was found to be associated with the degree of grain boundary etching.

(xi) The etching effects at the grain boundaries, can in certain cases, persist from one austenising treatment to the next.

(2) The mechanism of temper brittleness can be explained by assuming that segregation of solute atoms to the grain boundaries takes place while the steel is austenitic. This leads to precipitation (mostly at the grain boundaries) when the steel is suitably heat treated. Nearly all the experimental results can be explained without further major assumptions.

(3) The nature of the precipitate causing temper brittleness is not known, and there is insufficient direct evidence to put forward any one compound as the precipitate. The possibility of ascertaining the composition of the precipitate has been discussed, and it is shown that only by considerable development of certain existing techniques is there any likelyhood of accomplishing this. It is also thought that no real advance in the subject can be made on the theoretical side without this identification.

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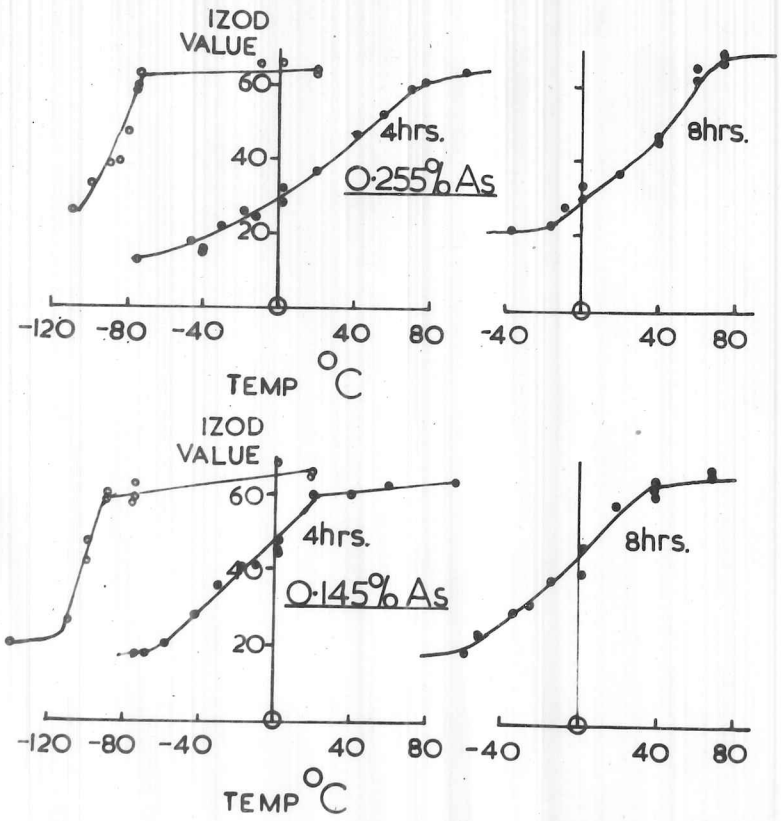
# APPENDIX A

## TRANSITION CURVES.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20
4hrs.
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8hrs.
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-40 40 80
TEMP °C
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0·145% As
8hrs.
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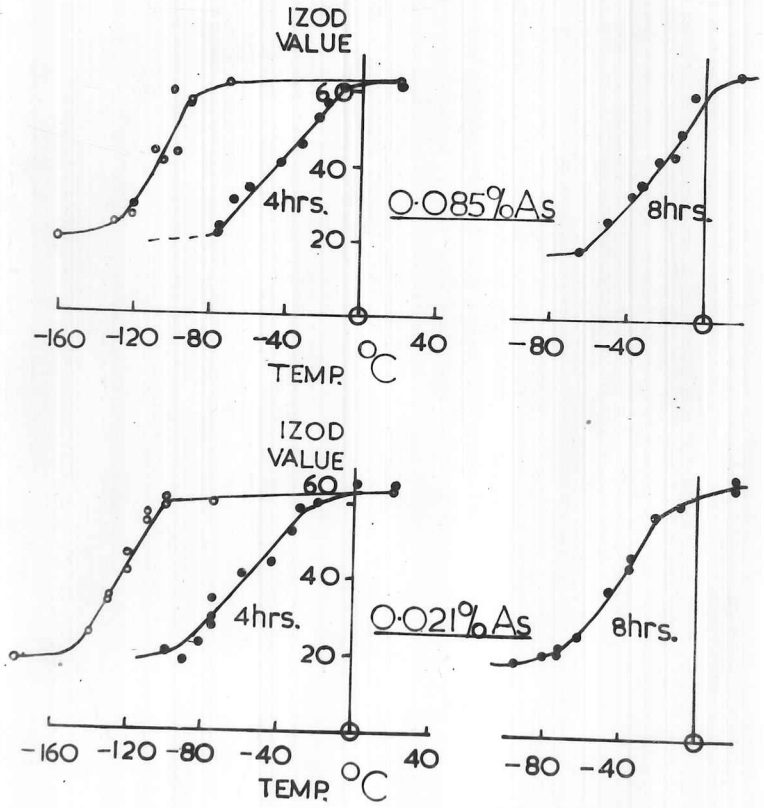
-40 40 80
TEMP °C
E.N.23

Fig. A1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-80 -40
TEMP °C
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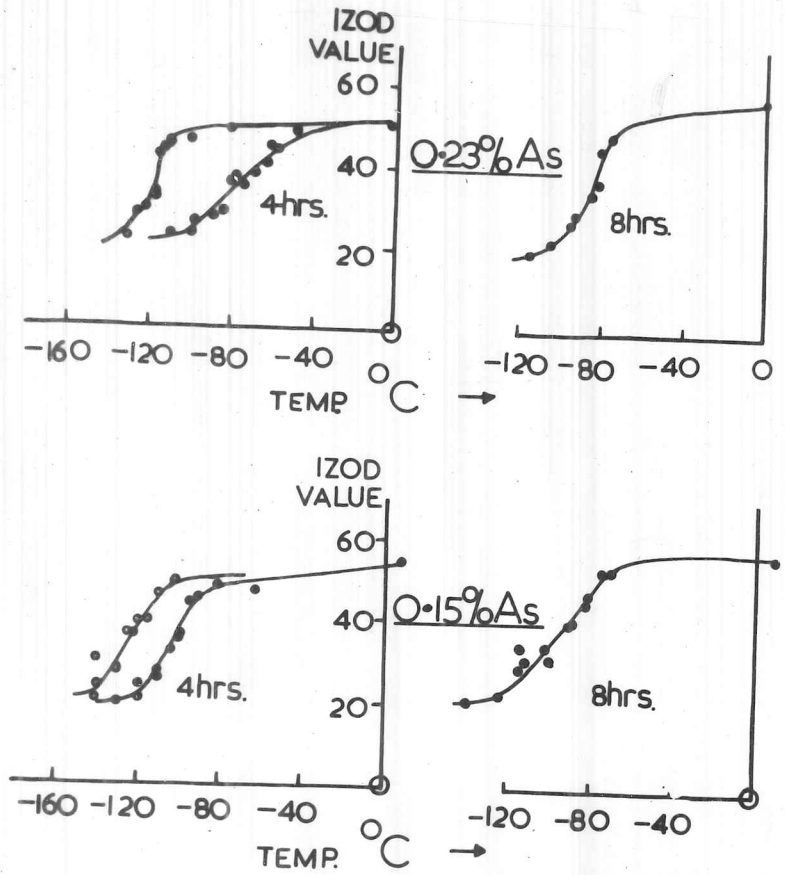
TEMP °C
E.N.23

Fig. A2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8hrs.
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TEMP. °C
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40
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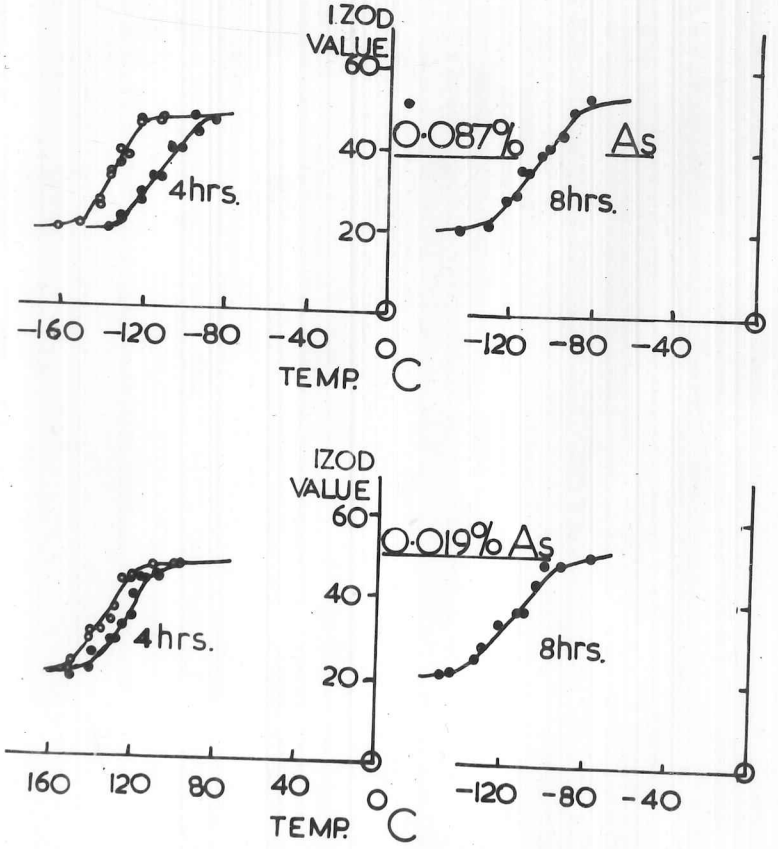
-120 -80 -40
TEMP. °C
EN 23 + Mo.

Fig. A3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TEMP. °C
IZOD VALUE
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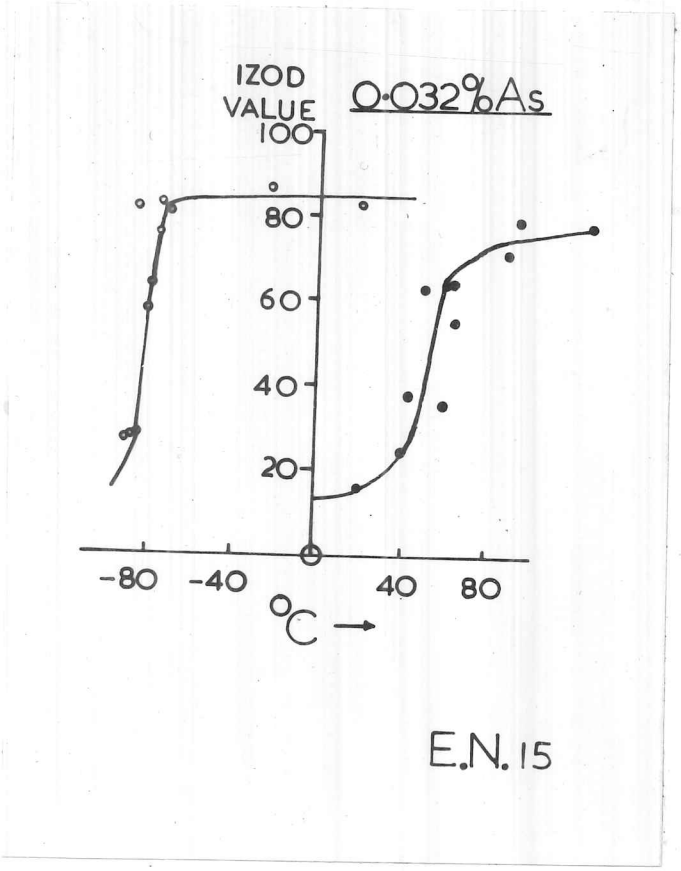
4hrs.
8hrs.
160 120 80 40
-120 -80 -40
TEMP. °C
EN 23 + Mo

Fig. A4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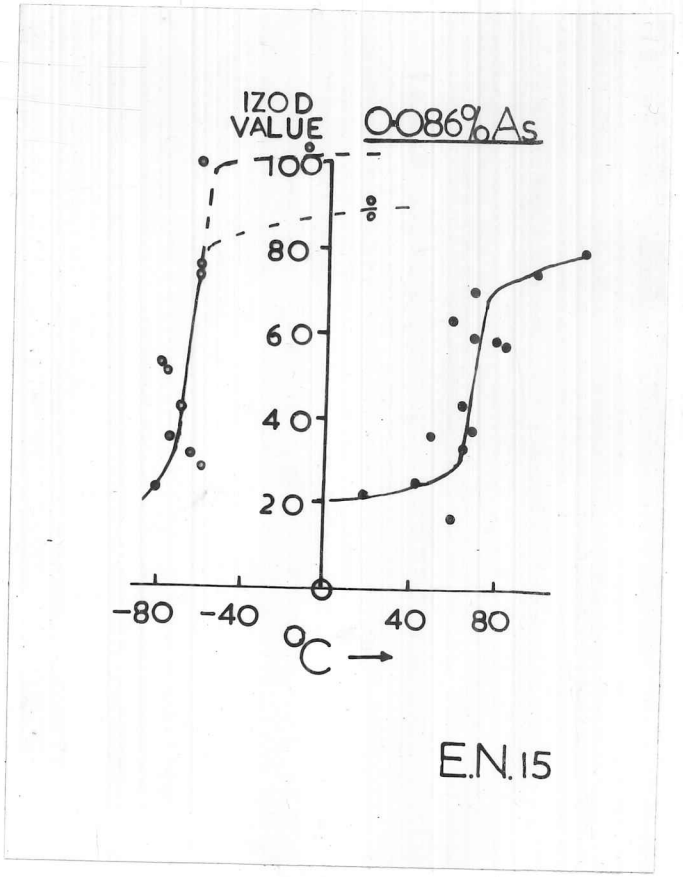
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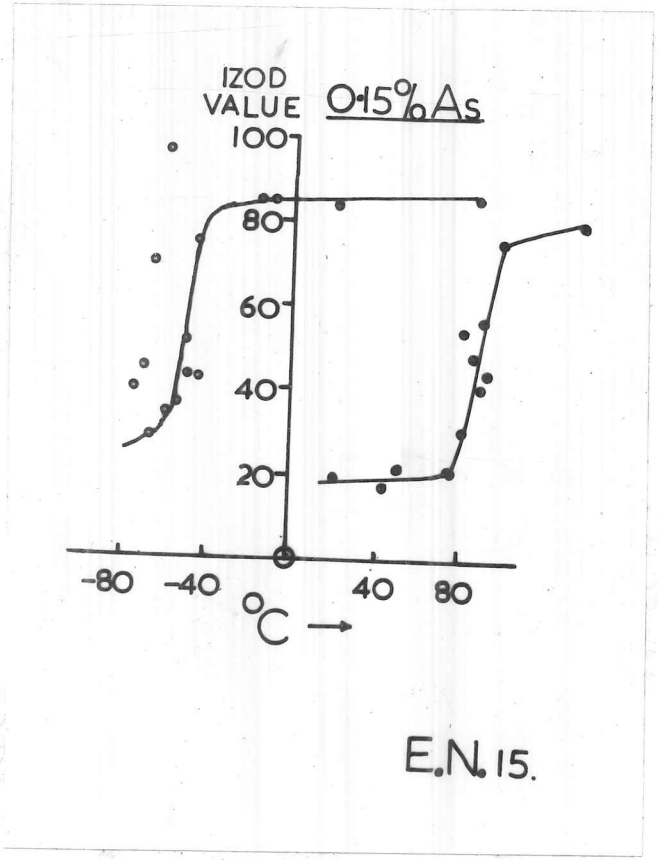
(b)

Fig. A5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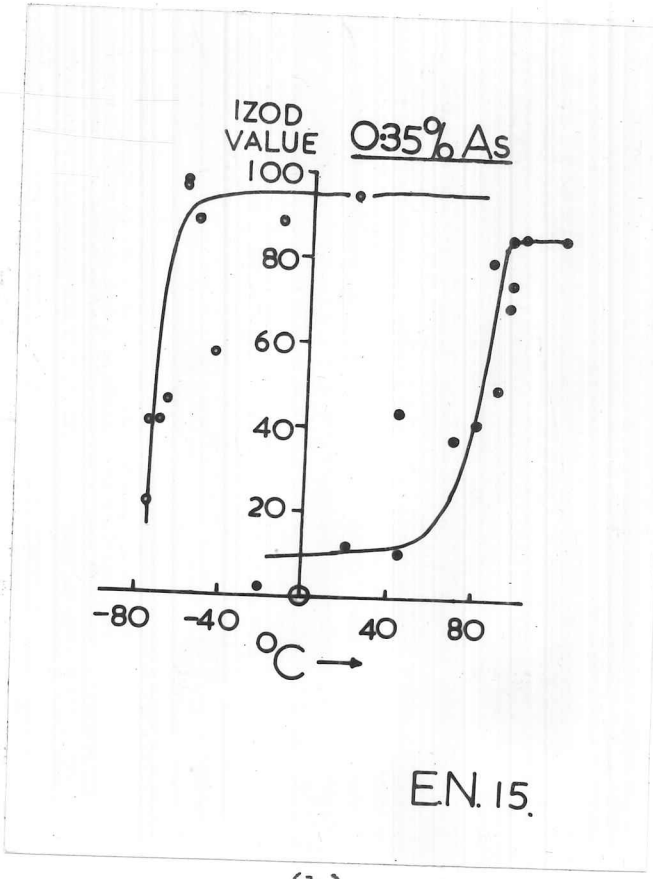
E.N. 15.

(a)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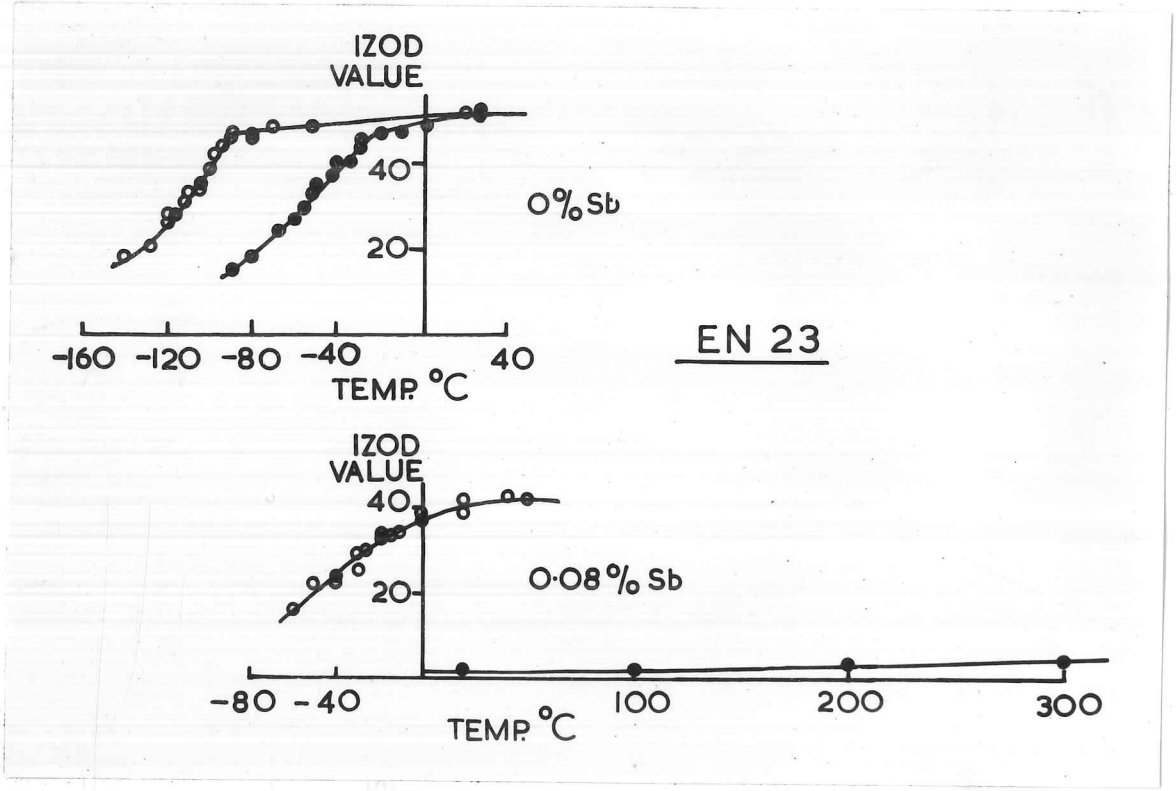
°C →
E.N. 15.

(b)

Fig. A6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EN 23
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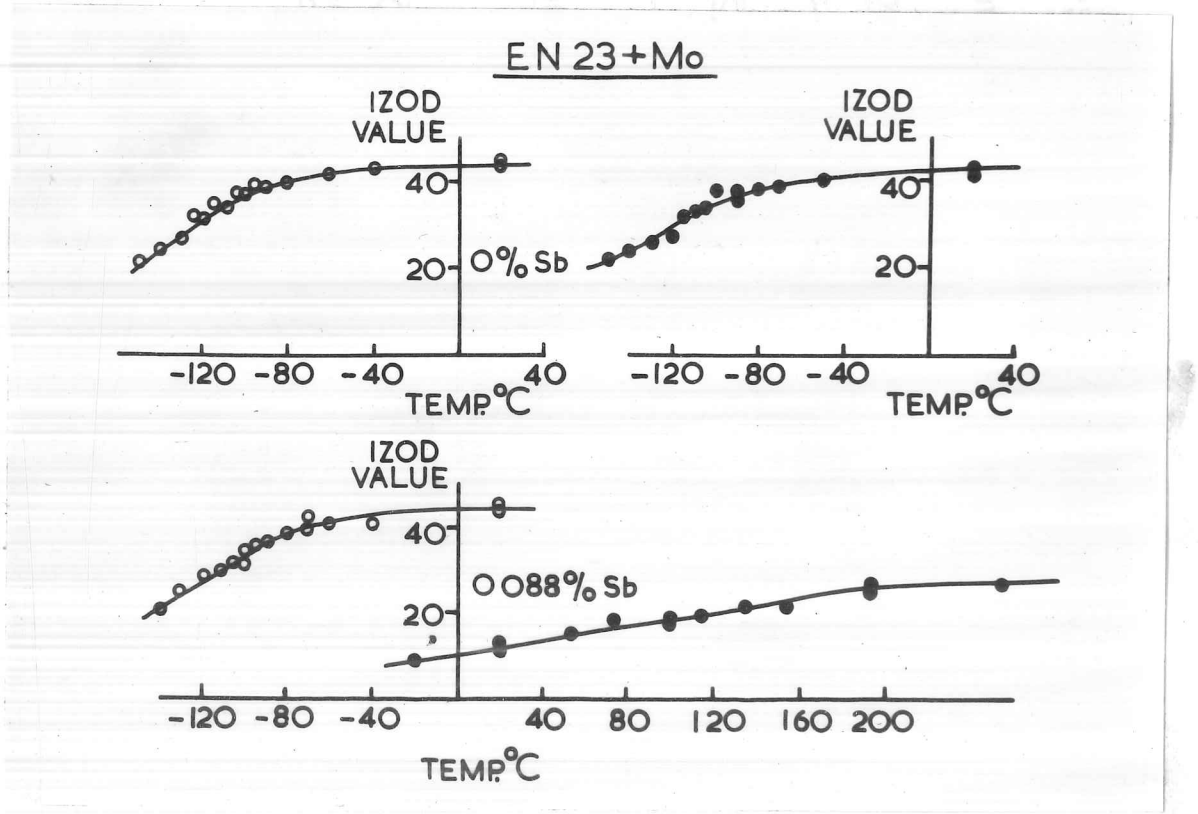
TEMP. °C

Fig. A7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TEMP. °C
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TEMP. °C
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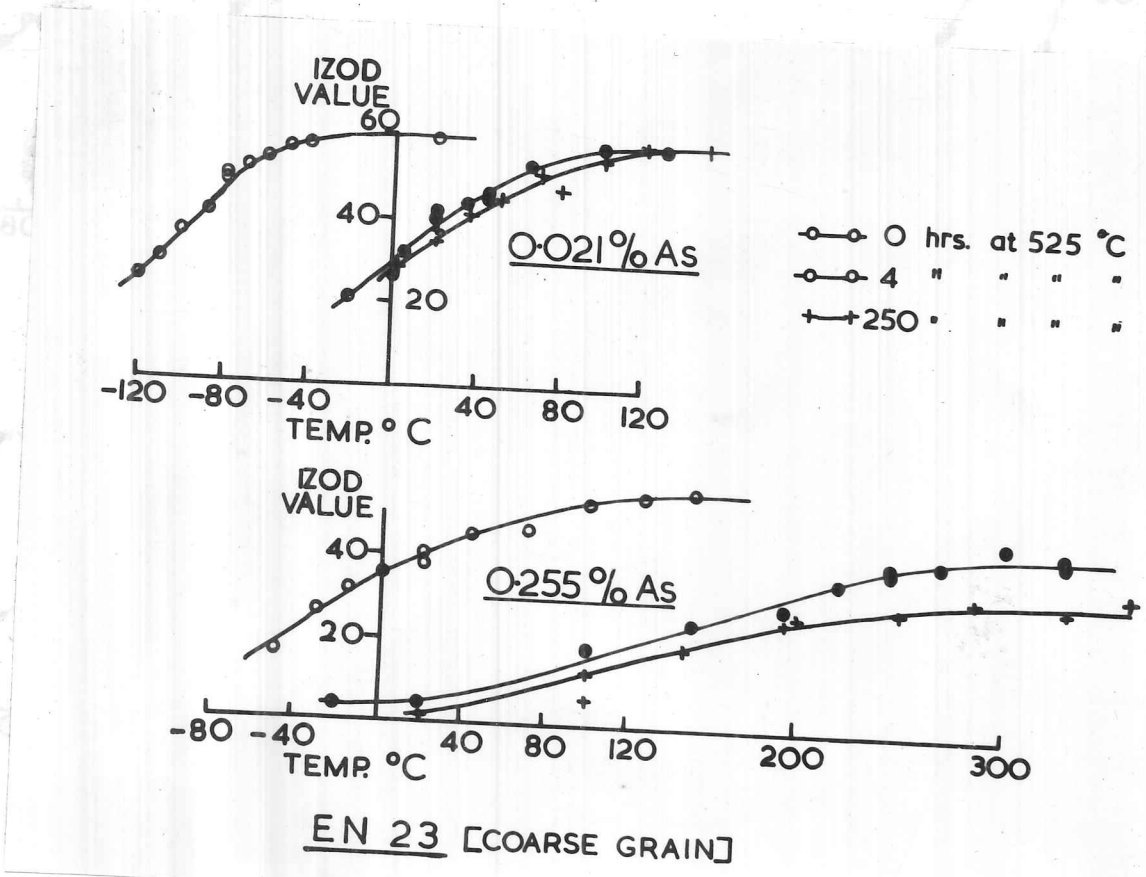
TEMP. °C

Fig. A8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TEMP. ° C
0 hrs. at 525 °C
4 " " " "
250 " " " "
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40 80 120 200 300
TEMP. °C
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Fig. A9

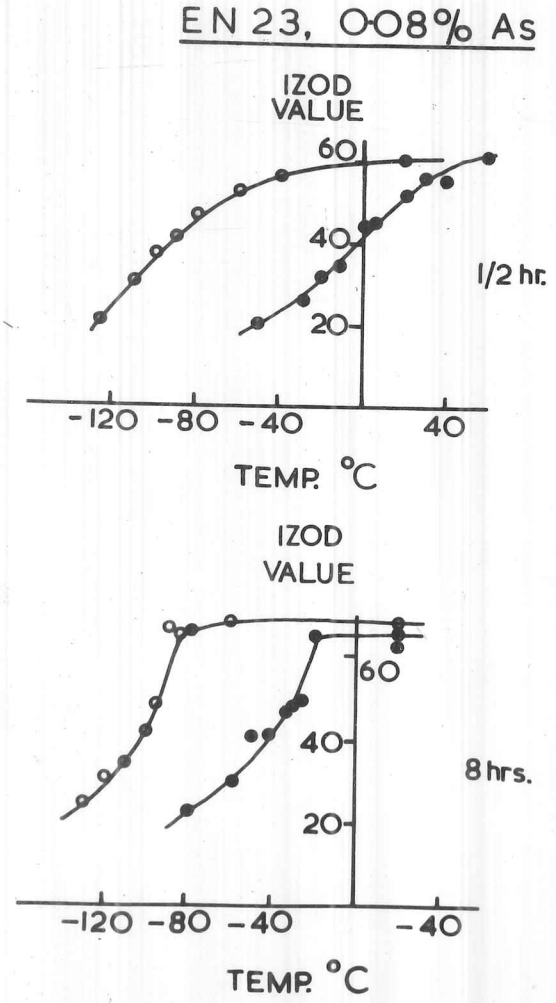



Fig. A10

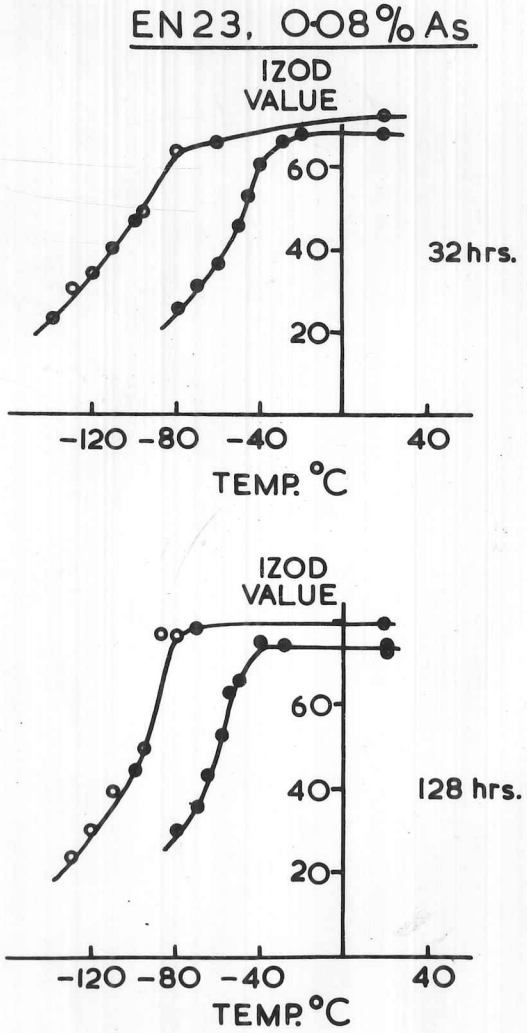



Fig. A11

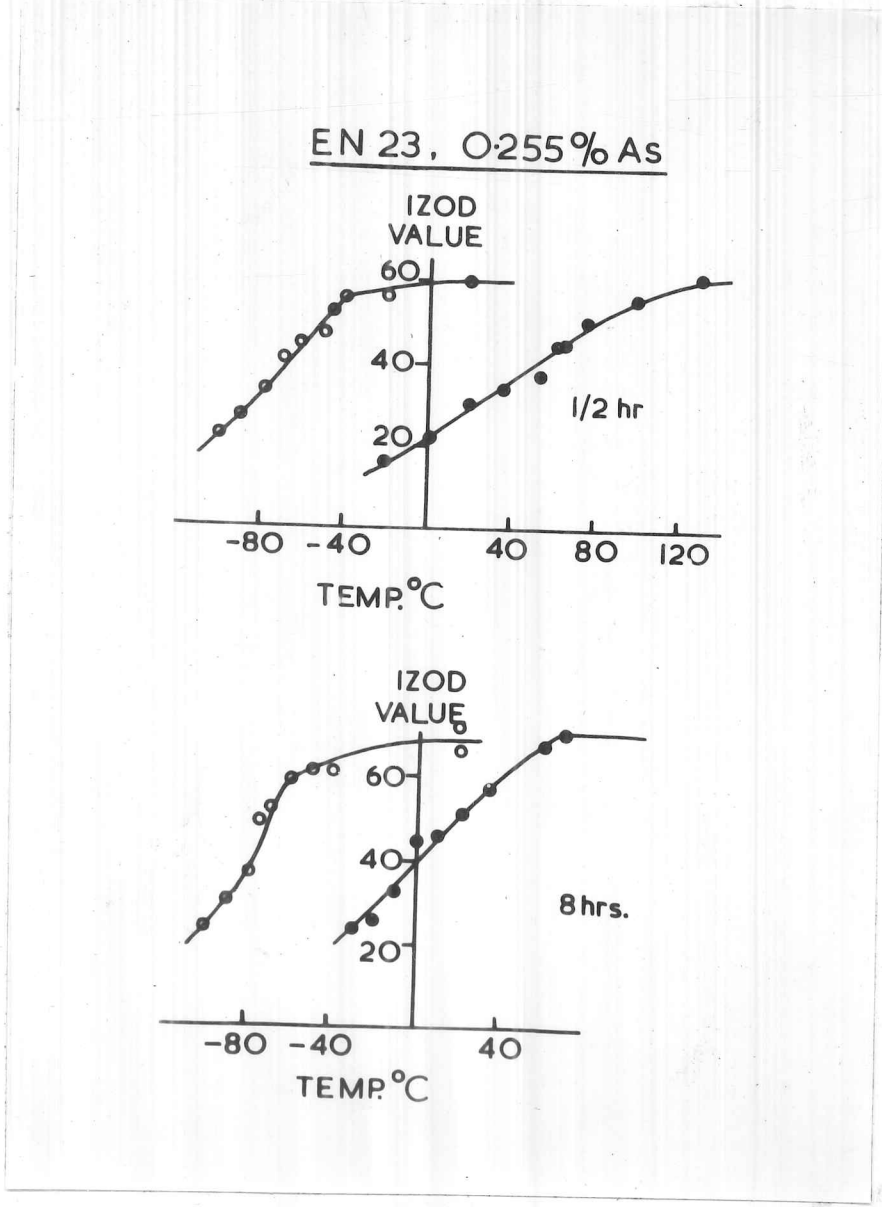



Fig. A12

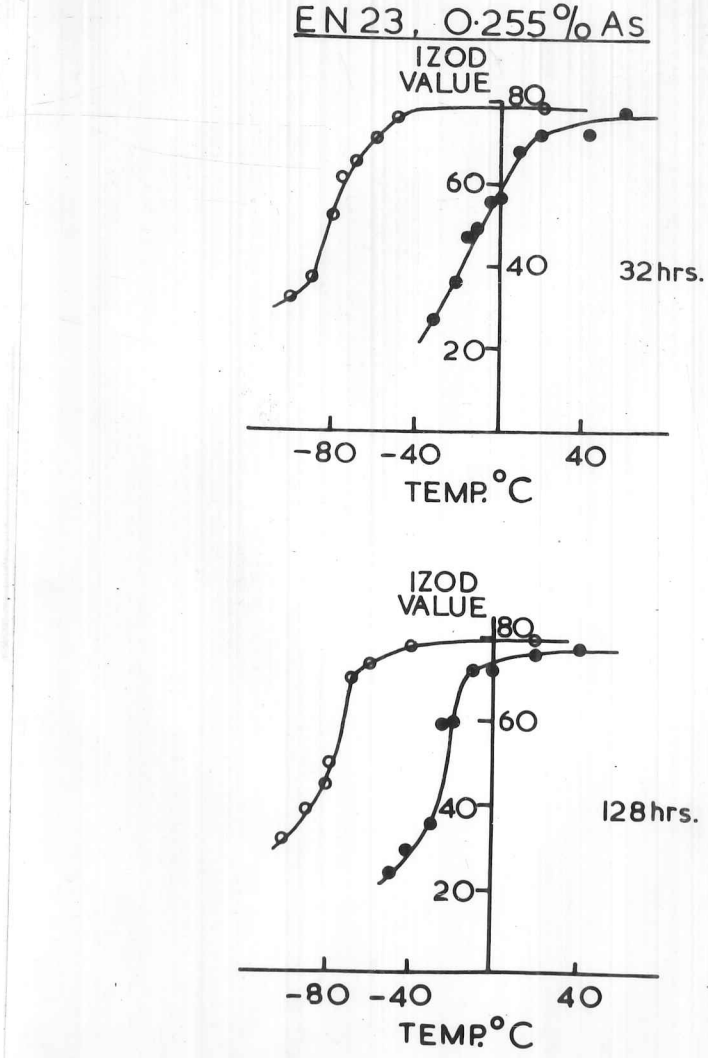



Fig. A13

# APPENDIX B

## THE X-RAY METHOD.

## X-RAY METHOD.

By P.B. Hirsch, M.A., Ph.D.

A back-reflection photograph was taken with an X-ray beam of ca. 1 mm. diameter (Co K$\alpha$ radiation). The photograph consists of arcs along Debye-Scherrer rings. Each arc corresponds to a region of strong preferred orientation in the material. The number of arcs ($N_1$, $N_o$) on the Debye-Scherrer rings on two photographs of different exposures ($T_1$, $T_o$) were counted and the mean volume V of material contributing to one arc could be determined from the relation

$$\frac{N_1 - N_o}{A \log_{10}\left(\frac{T_1}{T_o}\right)} = \frac{2.3\, p \cos\theta}{2\mu(1 - \sec 2\theta)} \frac{1}{V} \cdot (d\theta + \Delta)$$

where A is the area of the beam at the specimen (measured photographically); $p$ is the multiplicity factor for the reflecting planes; $\mu$ is the absorption coefficient; $\theta$ the Bragg angle; $d\theta$ is the divergence of the X-ray beam (measured photographically); $\Delta$ is the range of angle over which the region can reflect. The quantity $\Delta$ was determined from the extent of the arcs along the ring using the relation

$$\sin\tfrac{1}{2}\Delta = \cos\theta \cdot \sin\tfrac{1}{2}\gamma$$

where $\gamma$ is the angle subtended by the arc at the centre of the diffraction ring.

The mean diameter of the regions of preferred orientation was found to be ca.60$\mu$, while the range of misorientation was ca.3°. It is of interest to note that as the diffraction rings were quite sharp the size of the ferrite particles (forming the aggregates of diameter ca.60$\mu$) was expected to be ca.1$\mu$, in agreement with the metallographic evidence.

Further details about the method of counting spots and its application to the study of substructure in materials may be found in the following references:-

J.N. Kellar, P.B. Hirsch, and J.S. Thorp. Nature (London) 1950, Vol. 165, p.554.

P. Gay and P.B. Hirsch. Acta Cryst. 1951, Vol.4, p.284.

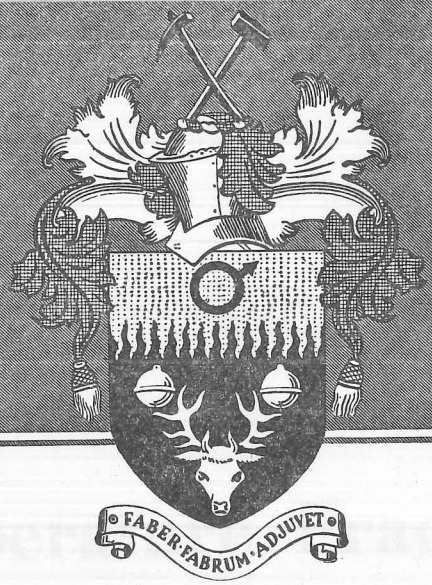
P.B. Hirsch, Ph.D. Dissertation, University of Cambridge, 1950.

# APPENDIX C

## "LOW TEMPERATURE FRACTURES IN TEMPERED ALLOY STEELS"

by

A.R. ENTWISLE., B.A.




# LOW-TEMPERATURE FRACTURES IN TEMPERED ALLOY STEELS

By

A. R. ENTWISLE, B.A.



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# Low-Temperature Fractures in Tempered Alloy Steels

BY A. R. ENTWHISTLE, B.A.

# Low-Temperature Fractures in Tempered Alloy Steels

*By A. R. Entwisle, B.A.*

**SYNOPSIS**

Low-alloy steels susceptible to temper-embrittlement may show fracture at low temperatures with either a cleavage or an intergranular fracture, depending on the heat-treatment. The cleavage type of failure is shown to be related to the original martensite structure produced on quenching. Under certain conditions both types of failure can occur in the same fracture. Plain-carbon steels similarly heat-treated show cleavage but not intergranular fracture.

As part of an investigation of temper-brittleness, a study has been made of fractures of plain-carbon and low-alloy steels at low temperatures, the latter steels being in various states of temper-embrittlement. Previously, McClean and Northcott[1] examined low-temperature types of fracture in tempered steels in the ' tough ' and brittle condition, and noted the ' leaf-like ' structure of the fracture of the tough steel. The present work is a more detailed examination of the fractures obtained under experimental conditions that produce brittle fracture.

## EXPERIMENTAL TECHNIQUE

The low-alloy steel used for most of the investigation was type En 23, as follows :

*Chemical Composition*, %

| | | | |
|---|---|---|---|
| C | 0·41 | As | 0·085 |
| Si | 0·70 | Cr | 0·66 |
| Mn | 0·43 | Ni | 3·01 |
| S | 0·0295 | Mo | 0·05 |
| P | 0·024 | | |

Specimens of this material (0·45-in. rounds) were oil-quenched from 1250° C., tempered for 1 hr. at 640° C., and subsequently embrittled at 525° C. The high quenching temperature was used so as to develop a large austenite grain size to facilitate metallographic observations. The actual size established was rather mixed, but was in the range 0–3 A.S.T.M. After being notched, the specimens, which were Izod impact test pieces, were fractured at — 180° C., and the fractures were then examined at × 40 and × 400 magnifications.

Paper MG/A/91/51 of the Alloy Steels Research Committee of the Metallurgy (General) Division, received 3rd April, 1951. The views expressed are the author's and are not necessarily endorsed by the Committee as a body.

Mr. Entwisle is in the Department of Metallurgy of Cambridge University.

## MICROSCOPIC EXAMINATION

Examinations of the non-embrittled material showed that the fractures were almost completely of the cleavage type, with a very small number of intergranular surfaces. At low magnifications, the fractures were characterized by the sudden changes in direction of fracture at the grain boundaries, and by the austenite grains retaining their individuality in the fracture (*see* Fig. 1). The actual cleavage facets were of the characteristic feathery shapes reported by McLean and Northcott (*see* Fig. 2).

Many areas were observed with structures having many facets in the same plane, similar to that shown in Fig. 3. These facets were considerably larger than the ferrite grain size, which was about 0·8 μ. The similarity between the fracture structure and the microstructure of the specimen seemed to indicate that the 'feathery shapes' corresponded in some way to the martensite plates before fracture. Figure 4 shows the microstructure. (It is shown after embrittlement so that the austenite grain size can be determined.) These areas had fractured in the same plane, indicating that all the ferrite grains over quite large



Fig. 2

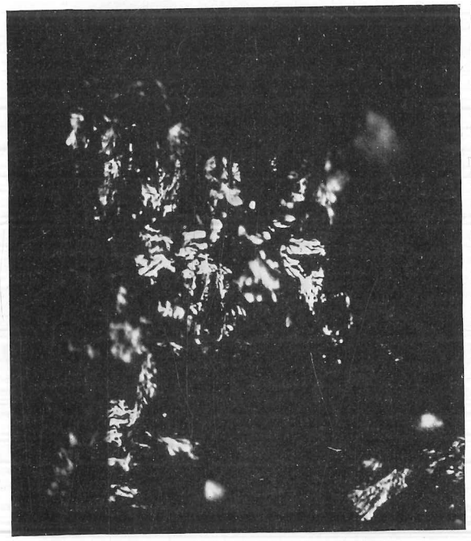


Fig. 4

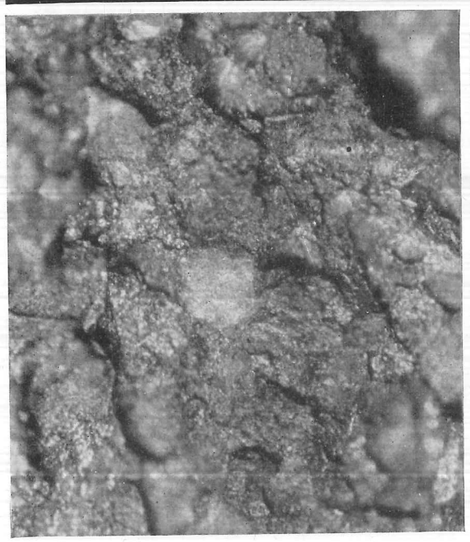


Fig. 1

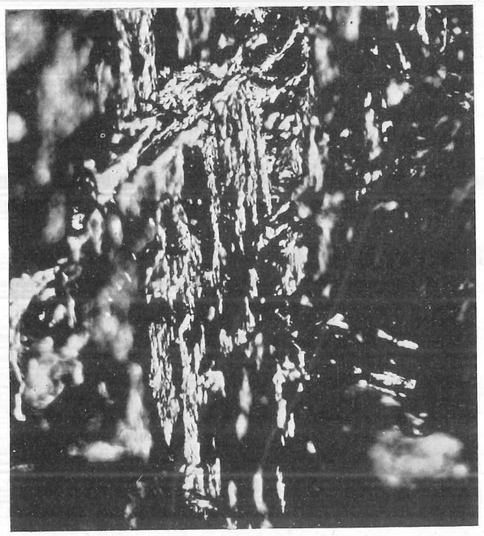


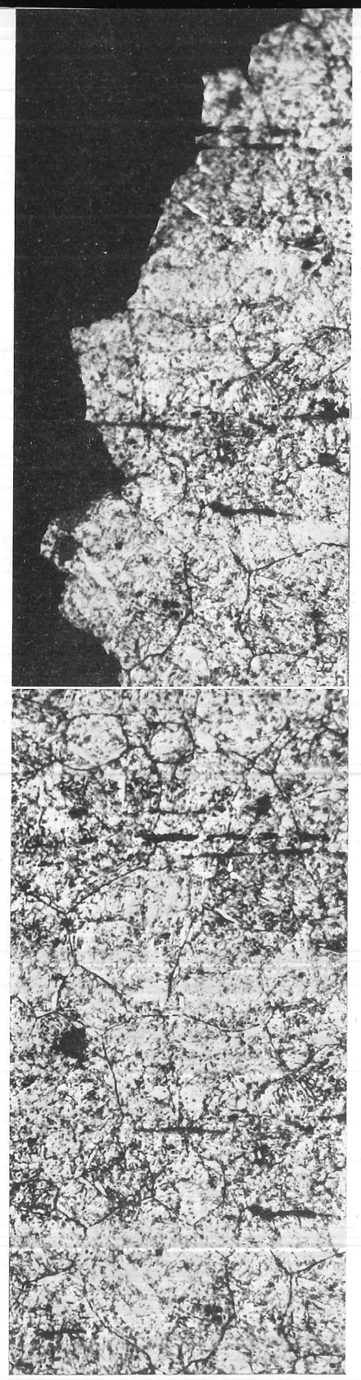
Fig. 3

Fig. 2—Same fracture as in Fig. 1 × 420 (Vertical illumination)

Fig. 4—Microstructure of ' tough ' steel after embrittlement × 420

Fig. 1—Low Temperature fracture of ' tough ' Ni-Cr steel × 72 (Dark field illumination)

Fig. 3—Same fracture as in Fig. 1 × 420



(b) After fracture

(a) Before fracture

Fig. 5—Microstructure of section of embrittled Ni–Cr steel

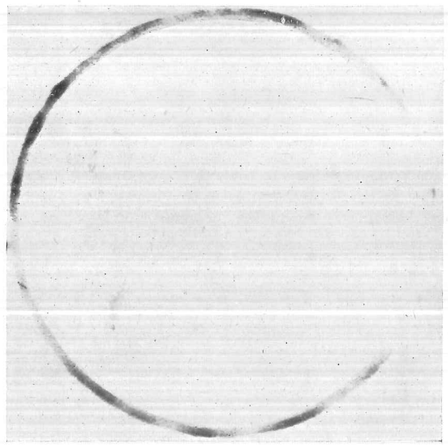


Fig. 6—Back reflection photograph using CoK$\alpha$ radiation





regions had approximately the same orientation. These regions would seem to correspond with the areas of uniform orientation of the martensite before fracture. Any one austenite grain is thought to transform to a limited number of these regions of uniform martensite orientation.

These ideas were confirmed by using an X-ray back-reflection technique on a polished, etched specimen (*see* Appendix). The X-ray work showed that the ferrite grains were assembled in aggregates of about 60 $\mu$ dia. in which the ferrite grain orientations were substantially the same. The actual misalignments are of the order of 3°. As the mean equivalent austenite grain diameter was about 100 $\mu$, these results indicate that any one austenite grain transforms to about eight orientations of martensite, and not to a random distribution of the 24 orientations as might be expected from the Kurdjumov-Sachs relationship.

The microstructure and appearance of the fracture can therefore be correlated. The tempered martensite of plain-carbon steels shows a similar type of fracture. For a very small austenite grain size (A.S.T.M. 8), the fracture studies indicate that the martensite transformation is even more restricted, as each grain appears to form only two or three facets.

## EXAMINATION OF FRACTURED IMPACT SPECIMENS

The fracture of temper-embrittled alloy steels has long been thought to be intergranular with respect to the prior austenite grains.[2] This was further demonstrated in the following way :

An Izod specimen (square section) of a severely embrittled sample of the En 23 steel was made in two halves. The plane of separation was along the longest axis of the specimen perpendicular to the plane of the notch and parallel to the direction of impact. The two surfaces at the dividing plane were polished, and etched with an ethereal solution of picric acid and CTAB[1] to reveal the austenite grain size. The microstructure near the notch was then photographed. The two specimen halves were bolted tightly together, and the composite specimen was fractured at — 180° C. In this way deformation at the polished surfaces was restricted. After fracture, the microstructure at the fractured edge was photographed and compared with the photographs taken previously. Plastic deformation had been almost eliminated, and it was possible to trace the course of the fracture across the specimen. It was found to be substantially intergranular with respect to the prior austenite grains. Figure 5*a* shows a typical area before fracture, and Fig. 5*b* the same area after fracture. Portions of the edge that are slightly out of focus indicate regions of plastic deformation. The free surface is not favourable for propagating brittle fracture, and where grain boundaries are unfavourably orientated with respect to the advancing crack, some deformation takes place before fracture.

Examination of the surface of the fracture rather than the section shows the characteristic gently curved facets associated with intergranular failure. The surfaces are rough and contain many small particles which were thought by Nutting[3] to be carbides. When examined in polarized light, the larger particles (at the grain edges) are found to have the same optical properties as the larger grain-boundary carbides in the microsection (only the larger particles are suitable for observation). The grain-boundary carbides are larger than the average particle size, which is consistent with the observation that the particles on the fractured surface are larger than average.

The effect of progressive embrittlement at 525° C. on the fracture at — 180° C. was studied. After 15 min. at 525° C. the fracture was found to be about 50% intergranular ; after 45 min., about 80% intergranular ; and after about 2 hr. it was almost exclusively intergranular. Since the 15-min. treatment would only lead to a change in transition temperature of the order of 10° C. it is evident that the fracture changes from one type to the other quite rapidly ; after a quite small change in transition temperature subsequent changes must result from the increasing ease of intergranular fracture and not from increasing proportions of intergranular failure. This is being studied further, but it appears that the low-temperature brittle fracture of an alloy steel might be used as a sensitive test for detecting small amounts of temper-embrittlement. If the intergranular fracture is taken as the criterion of temper-embrittlement, then the test can be used to determine whether or not changes of transition temperature in steels are associated with temper-brittleness. At present, all adverse changes in transition temperature in low-alloy steels are usually ascribed to temper-brittleness, but this may not be true.

With very fine-grained steels (A.S.T.M. 8–9), it is more difficult to discriminate between the two types of fracture, because all the phenomena are on a smaller scale, and it is not easy to compensate for this by increasing the magnification.

In the mixed fractures (*i.e.*, cleavage plus intergranular) there is a tendency for the intergranular facets to occur more frequently near the notch, and for the cleavage fracture to predominate at points away from the notch. The type of failure at any given place is probably controlled by the orientation of the grain boundary, the stress conditions, and the non-uniformity of the precipitation, but the effect of each is not known. The surface-active etching reagents (CTAB etc.) give non-uniform etching effects, and uniform precipitation plays an important part as no cleavage facets appear in severely embrittled specimens.

The information obtained from these experiments was used to determine, from a study of the fracture of plain-carbon steels (tempered martensite), whether they were susceptible to temper-brittleness, as had been suggested by Jaffe and Buffum.[4]

Specimens of a steel (B.S. En 8) containing 0·4% of C, and 0·65% of Mn were used. They were quenched in brine from 1000° C., tempered for 1 hr. at 630° C., and water-quenched. Some were then ' embrittled ' by heating at 480° C. for 24 hr. After breaking notched samples in liquid oxygen, the fractures were examined. In both sets of specimens the fracture was predominantly cleavage, but the specimen treated at 480° C. did contain a small amount (not more than 5%) of intergranular facets. This refutes the hypo-

thesis of Jaffe and Buffum, that plain-carbon steels are highly embrittled, even when quenched after tempering above 600° C., and suggests that the high transition temperatures of plain-carbon steels are not a result of temper-embrittlement.

## DISCUSSION

As far as is known, a prior austenite grain boundary in tempered martensite is characterized by :

(i) Large carbide particles
(ii) Change in ferrite orientation with no simple relationship.

There are other possibilities, *e.g.*, segregation of alloying elements (which occurs in burning and overheating) and inclusions which will tend to be located in the grain boundaries. There will also be some form of precipitate located there when the material is embrittled. These characteristics are the normal grain-boundary features.

The experimental evidence shows that a tough steel when fractured in liquid nitrogen has a special type of cleavage fracture. This is shown to be associated with the structure of the ferrite (which is derived from the martensite). The ferrite grains (about 1 μ) are in groups of about 50 μ dia. (for this particular coarse austenite grain size) in which they all have the same orientation. There is microscopic evidence that the boundaries of these regions are characterized by carbides that are larger than average, and are thus similar to the austenite grain boundaries. This indicates that the effective ferrite grain size is 50 μ rather than 1 μ (*i.e.*, A.S.T.M. grain size 6).

As the austenite grain size decreases, so the size of the orientated regions decreases. Thus, for A.S.T.M. grain size 9, the ferrite regions are size 10. It may be the variation in size of these ferrite areas, together with the change in particle-size distribution of the carbides, that explain the effect of austenite grain size on the properties of tempered steels.

The intergranular fracture is shown to be a sensitive criterion for temper-embrittlement. The change from cleavage to intergranular fracture is shown to be continuous, but rapid. The mixed fractures are important, since they demonstrate that discontinuous embrittlement is sufficient to raise the transition temperature. This emphasizes that the transition temperature for any given specimen represents an average value for the whole specimen, and that fracture is easier in some regions than in others.

The intergranular fracture of temper-brittle steels is interesting in two respects :

(i) Because of the peculiar nature of the grain boundaries involved
(ii) Because of the localized precipitation effects.

The limited form of the precipitation may show that it is initially due to some segregation taking place while the steel is austenitic. This can cause localized precipitation on subsequent quenching and tempering.

## Acknowledgments

The author thanks Professor G. Wesley Austin for his advice and encouragement, and Mr. G. C. Smith of the Department of Metallurgy, Cambridge University, for much helpful discussion. The steel used was kindly supplied by Mr. H. Bull, of Brown-Bayley's Steelworks, Ltd. The work was financially supported by B.I.S.R.A.

# APPENDIX

## X-Ray Method

*By P. B. Hirsch, M.A., Ph.D.*

A back-reflection photograph was taken with an X-ray beam of about 1 mm. dia. (CoKα radiation). The photograph consists of arcs along Debye-Scherrer rings (Fig. 6). Each arc corresponds to a region of strong preferred orientation in the material. The numbers of arcs ($N_1$, $N_0$) on the Debye-Scherrer rings on two photographs of different exposures ($T_1$, $T_0$) were counted and the mean volume $V$ of material contributing to one arc could be determined from the relation :

$$\frac{N_1 - N_0}{A \log_{10}(T_1/T_0)} = \frac{2 \cdot 3p \cos\theta}{2\mu(1 - \sec 2\theta)} \cdot \frac{1}{V} \cdot (d\theta + \Delta)$$

where $A$ is the area of the beam at the specimen (measured photographically) ; $p$ is the multiplicity factor for the reflecting planes ; $\mu$ is the absorption coefficient ; $\theta$ is the Bragg angle ; $d\theta$ is the divergence of the X-ray beam (measured photographically) ; $\Delta$ is the range of angles over which the region can reflect. The quantity $\Delta$ was determined from the lengths of the arcs along the ring using the relation

$$\sin\tfrac{1}{2}\Delta = \cos\theta . \sin\tfrac{1}{2}\gamma$$

where $\gamma$ is the angle subtended by the arc at the centre of the diffraction ring.

The mean diameter of the regions of preferred orientation was found to be about 60 μ, while the range of mis-orientations was about 3°. It is of interest to note that as the diffraction rings were quite sharp the size of the ferrite particles (forming aggregates of diameter about 60 μ) was expected to be 1 μ, in agreement with the metallographic evidence.

Further details about the method of counting spots and its application to the study of substructure in materials have been given elsewhere.[5, 6, 7]

Dr. Hirsch is at the Crystallographic Laboratory, Cavendish Laboratory, Cambridge.

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